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Geogenic and Pedogenic Inheritance of Arsenic, Antimony, Selenium and Tellurium in Poorly Developed and Metamorphic Soils

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Abstract

The content of arsenic, antimony, selenium and tellurium in soils from a territory with natural and man-caused load, located in the range of the Old Quaternary proluvial plume in the northeastern part of the Sofia valley, was studied. The contents have been determined by LA-ICP-MS, together with those of more than 45 chemical elements, for the purpose of future remediation and study of the impact of natural and man-made factors on the geochemical relationships of the elements in the specific soil environment. The studied soil types are Regosols and Cambisols, most of which have been changed and classified as Technosols (*IUSS Working Group WRB*, 2015, Teoharov et al., 2019, Stoykova, 2021) under the influence of industrial waste from the former Kremikovtzi metallurgical plant. Very high contents of the groups of elements Te - Se and As - Sb have been established, which are inherited from the soil - forming rocks with predominant, respectively syenite or ore material. The content of arsenic in Technosols is on average 4 times higher than the maximum permissible concentration of metalloid in industrial soils, and the arsenic in the control profile of Cambisols exceeds 1.5 times the norm for the maximum permissible concentration for arable land. The processes of overwetting, acidification and microbiological activity are the factors that influence the redistribution of the four elements in the soil environment. Contamination with agglomeration dust leads to the accumulation of antimony in the spolic horizon, where it is associated with a number of heavy metals. Its more metallic character is reflected in the statistically significant high positive correlation with iron - $r(\text{Sb-Fe}) = 0.85$, which shows only this element.

Keywords: arsenic, antimony, contamination, Cambisols, Regosols, selenium, tellurium, Technosols

Introduction

Arsenic (As), antimony (Sb), selenium (Se) and tellurium (Te) are chalcophilic elements of the p-block of the Periodic Table, satellites (As, Sb) or analogues (Se, Te) of sulfur (Stefanova, 2005). In the primary endogenous environment they are concentrated in sulfides, related minerals and sulfosols, and in the exogenous environment, like sulfur, they are oxidized relatively easily (Stefanova, 2005, Plant et al. 2003, Fersman, 1939) and in the form of variously charged oxygen radicals compounds are involved in active soil metabolism. Soil macro and microbiome, including man, are directly influenced by the excess content of

these elements (Sadiq, 1995, Denys, 2009, Missen, 2020, Cuvaradic, 2003). Their study is of interest to soil science not only because of their toxic effects on living organisms, but also because of the food needs of selenium, which is a trace element essential for organisms.

In the context of the specific geological and ecological situation on the territory of the former Kremikovtzi MP and beyond, the study of these four elements serves purely scientific interests, as processes can be identified - natural and technogenic, affecting their distribution in the soil environment. The soils subject to the present study were developed on proluvial rocks containing materials of diverse geological origin, naturally enriched in metals and metalloids, primarily gold (Stoykova, 2021). The proluvial rocks, shaped like proluvial cones connected in an extensive proluvial plume, are the result of drainage through ravines of two feeding provinces (tentatively called *western* and *eastern*) that operated during the Pleistocene. They are poorly fused gravels with sandy-clay matrix and alternating grains of sand, gravel and clay horizons. They contain rock fragments and deposited products of Paleozoic argillites, siltstones, lydites and others. with varying degrees of metamorphism, carbonate and clay-carbonate Triassic and Jurassic sediments (Angelov et al., 2008), potassium-alkaline magmatic rocks from the Buhovo-Seslavitzi pluton (Dyulgerov, 2005), ore rocks and ore minerals from the Buhovo uranium deposit (Kalaydzhiev, 1993). Due to their loose structure and proximity to the mountain slope, they are relatively easy to weather and should have lost much of their primary minerals. According to Stoykova (2021), the technogenic situation in the district and the reported alkalization also invariably influenced the geochemical relations of the elements sensitive to the parameters of the environment, such as arsenic, antimony, selenium and tellurium.

The complicated technogenic situation is due to the nearly 50 years of operation of the former Kremikovtzi metallurgical plant, which is a conglomeration of heavy industry plants, located on an area of 24,000 m². Agricultural land around the plant has been the subject of many studies over the years. From them it can be concluded that the lands have high levels of heavy metals and arsenic around the plant, and with the removal of it only lead and arsenic remain exceeded (Faitondjiev et al., 2000; Shulin et al., 2007).

This publication is the only one that interprets the results for the content of arsenic, antimony, selenium and tellurium, as a group obtained together with data for more than 45 other chemical elements in soil profiles located near various factories inside the plant. External control profiles were also included in the study.

Materials and Methods

Soils from 15 profiles in the area of Kremikovtzi MC have been studied, incl. 11 from the territory of the plant - with man-caused influence and 4 controls in different directions outside it. The profiles are divided into a total of 6 geographical positions. In turn, the eleven profiles with man-made impact are grouped into three groups depending on the type of pollution, as well as the local geographical location:

- o In the middle parts of the western proluvial cone, in a border area with modern proluvium, rich in deposited limestones and potassium-alkaline magmatic rocks, mainly syenites (Terrain group I) - Profiles 1, 2, 3, 4 + 13c, 14c,
- o In the upper parts of the eastern proluvial cone, rich in deposited limestone and ore matter - (Terrain group II) - Profiles 5, 6, 7, 8.

o In the middle parts of the eastern proluvial cone - (Terrain group III) - Profiles № 9, 10, 11.

A number of standard soil analyzes were performed on the 15 soil profiles. In view of the large database, five man-made influences were selected (Profiles № 3, 6, 7, 8 and 11) and one control profile - № 13c, the most representative for each of the initially separated groups, which were subjected to additional chemical and mineralogical research, incl. LA-ICP-MS. The results of the chemical analyzes are an interpretation based on the parameters

o Average content,

o Linear Brave correlation coefficient (r). The statistical significance of the obtained coefficient is calculated by the formula $|r| \geq 3 * \sigma_r$, where $\sigma_r = (1 - r^2) / \sqrt{n}$, and “n” is the number of pairs in the correlation. After the calculations, it was determined that the correlation coefficients in the intervals $(-1 \div -0.5)$ and $(0.5 \div 1)$ (Rollinson, 1993) were statistically significant.

o Concentration coefficient (CC), calculated as the ratio between the content of the element in the specific horizon of the profile (K_e) to its content in the lowest horizon of the same profile (K_c) – K_e / K_c (Fersman, 1953; Stefanova, 2005). This coefficient makes it possible to identify accumulation and migration processes vertically, within the soil profile.

According to their genetic nature and the natural course of soil development, secondarily contaminated soils are divided into two groups: Cambisols - profile 3, profile 7, profile 13c and Regosols - profile 6, profile 8, profile 11. According to the changes that have taken place due to the influence of industrial materials, some of them are already classified as Technosols (Stoykova, 2021).

Morphologically, the studied soils are reddish in color (50% of all samples have a hue of 5 YR), with high fragmentation, naturally or artificially overlapped. Cambisols have well-formed genetic horizons, and Regosols have a layered profile structure. Soil-forming sediments are reached everywhere - alternating gravel, sand and clay layers. Vegetation in the technogenic profiles is scarce or absent, except for one secondary afforested with acacia profile (№ 1).

Results and Discussion

According to the results obtained, the average content of the discussed elements in the studied soils is much higher, compared to selected reference values (Kabata-Pendias, 2011) - $Te (56x) \gg As (25x) > Se (24x) \gg Sb (10x)$. The determined average contents are (in $\mu g / g$) As – 170.66 ($409.34 \div 24.63$); Se – 10.56 ($14.25 \div 6.15$); Sb – 6.66 ($13.93 \div 3.13$) and Te – 4.49 ($7.03 \div 2.14$) (Table 1).

Of the four elements, the content of arsenic in soils is subject to state regulation, on the one hand as the most common of them, but also because of its anthropogenic contribution to the soil and its toxic properties, falling into it. The values obtained for this element exceed the trigger values from Regulation 3 / 1.08.2008 as follows: arsenic in Technosols is on average about 4 times above the maximum permissible concentration of metalloid in industrial soils ($40 \mu g / g$, Regulation 3 / 1.08.2008), and the arsenic in the control profile exceeds 1,5 times the established norm for the maximum permissible concentration in arable land ($25 \mu g / g$, Regulation 3 / 1.08.2008).

Table 1. Average contents of the studied elements, compared to world reference values (Kabata-Pendias, 2011), distributed by geographical area and by man-made pollution.

	Average in soils, ref. data	Average in this study	Mediana	Max	Min		Field group I	Field group II	Field group III		Control profile 13c, average
		$\mu\text{g/g}$									
As	6.83	170.66	150.22	409.34	24.63		97.80	247.56	144.93		37.21
Se	0.44	10.56	11.09	14.25	6.15		11.82	10.75	7.26		11.56
Sb	0.67	6.66	6.23	13.93	3.13		8.27	7.02	5.89		4.04
Te	0.08	4.49	4.95	7.03	2.14		5.58	4.43	2.91		4.81

The content of Te and Se is inherited from proluvial rocks enriched in syenite fragments, and that of As and Sb is bound to soil-forming materials enriched in ore minerals and sulfosols, arsenides and antimonides, some of the minerals accompanying uranium mining (Kalaydzhev, 1993). This statement is based on the higher measured values for the two groups of elements in the profiles of the respective terrain groups, which are formed on different soil-forming rocks - Te and Se in profiles №№ 3 and 13c of terrain group I and As and Sb in profiles №№ 6, 7, 8, 11, part of terrain groups II and III (Table 1, Table 2). The mechanism of Te concentration in alkaline magmatic rocks is known to science. Such rocks are associated with the largest deposits of tellurium and gold, in the form of tellurides, which are generally part of the ore (sulfide) fraction of accessory minerals (Kostov, 1993). Selenium, following its chalcophilic nature, is also concentrated in this fraction, where it forms its own selenides or replaces sulfur in metal sulfides (Kostov, 1993).

Natural and technogenic soil-forming processes are imposed on these soil-forming rocks, which lead to redistribution of the studied elements within the soil profiles.

The over wetting process covers the entire volume of profile 8 (Reductive Technosols, colluvic), combined with a strongly acidic soil reaction in the intermediate horizons (Table 2).

This has mobilized all four elements ($\text{CCTe} = 2.41$, $\text{CCSb} = 1.55$, $\text{CCSe} = 1.86$, $\text{CCAs} = 2.43$) (Fig. 1), which are known to be reduced in a reducing environment. easily reduce to neutral or weakly negatively charged mobile forms such as HAsO_2^0 , H_2AsO_3^- , HSbO_2^0 , SbO_2^- , Se (s), Te (s) (Sadiq, 1995, Denys, 2009, Missen, 2020, Plant et al., 2003) and hydrogenselenide anions (HSe^{2-}) - and hydrogenselenide (H_2Se^0), as a manifestation of the halogen nature of selenium (Cuvardic, 2003, Plant et al., 2003).

Antimony is an exception to the general trend in this example. The upward movement is to a lesser extent, and fixation is observed in the most acidic horizon AC_{III} (125 - 225 cm) and CC (1.55 and 1.53) for the surface and intermediate horizon, respectively. The behavior of antimony under these conditions reflects its metallic nature (expressed in the lowest energy of positive ionization Z^K among the four elements), by virtue of which in oxidation conditions it does not form charged oxygen radicals but solid mineral phases - Sb_2O_4 , Sb_2O_5 (Stefanova, 2005). They are adsorbed and incorporated isomorphically into the

poorly soluble Fe-Mn oxide and hydroxide structures crystallizing during the drought and oxidation period, thus gradually accumulating (Denys, 2009).

Table 2. Content of the studied elements, iron, manganese, sulfur and values of the main soil indicators.

Horizon / Depth, cm	Fe %	Mn mcg/g	S	As	Se	Sb	Te	pH / H ₂ O	CEC cmol/kg	Base-cation saturation, % % CEC	Total Carbon, %	Carbonates, %	Physical clay, %
Profile 3 Ekranic Spolic Technosols (Alcalic, Cambic, Chromic, Endoskeletal, Eutric, Toxic)													
Asp ₁	30-0	very black mass, agglomeration powder											
Aek	25-0	concrete flooring											
Asp ₂ k	0-50	13.25	9447.42	2726.75	79.10	10.35	13.93	4.68	8.4	22.3	100	0.63	9.1
B ₁	50-105	4.17	2117.42	1824.95	137.53	12.70	6.14	5.73	8	21.7	100	0.19	28.5
B ₂ w	105-170								7.5	20.6	100	0.11	40.5
1C	170-235	3.00	1239.74	1202.65	63.56	10.31	6.43	5.38	7.6	20.9	100	0.17	22.7
2Cg	235-347	4.65	1859.27	1872.34	111.01	13.92	6.58	6.52	8.2	26.3	100	0.54	50.6
Profile 6 Spolic Technosols (Alcalic, Chromic, Colluvic, Epicalcic, Eutric, Toxic)													
Asp ₁	30-0	granular and non-granular coke powder											
Asp ₂ k	0-40	4.28	9333.53	2383.79	170.70	11.40	6.31	4.83	9.2	27.6	100	0.4	5.9
aC _f	40-60	5.94	7918.97	1402.77	322.38	11.23	9.22	5.76	8	18.9	100	0	14.6
C ₁	60-110								7	18.2	96.2	0	18.4
C _{II}	110-160	5.21	4014.86	1534.74	275.37	10.94	7.78	4.87	6.9	16.9	94.7	0	36
C _{III} g	160-260	6.35	13075.71	2393.49	409.34	11.42	8.93	5.09	7.6	26.5	100	0.31	20.8
Profile 7 Spolic Technosols (Cambic, Chromic, Eutric, Gleyic, Toxic)													
Asp	10-0	coal dust											
Ak	0-38	4.73	6042.74	2515.69	196.01	12.58	5.58	6.53	8	26.8	100	0.18	38.4
AB	38-68								7.3	22.5	96.9	0.09	47.9
Bw(g)	68-110	4.96	2736.36	1112.65	162.90	8.85	6.14	2.14	7.6	22	100	0	43.7
BC	110-165								7.9	22.6	100	0.94	33
C	165-210	4.58	2737.84	1695.98	227.42	12.53	5.58	5.14	7.7	20.5	100	1.64	20.4
Profile 8 Spolic Reductic Technosols (Chromic, Colluvic, Eutric, Gleyic, Toxic)													
Asp	20-0	tar. tar fus. naphthalene											
AC _I g	0-40	5.36	3409.46	1728.74	333.90	13.34	7.85	5.51	7.9	19.3	100	0.14	22.7
AC _{II}	40-125								5.6	19.9	85.9	0.1	21.1
AC _{III}	125-225	5.09	1841.76	941.62	240.12	8.02	7.76	2.16	3.8	19.2	67.7	0.11	36.9
AC _{IV} g	225-400	4.91	2189.57	957.05	137.42	7.17	5.08	2.29	6.6	24.3	93	0	55.7
Profile 11 Spolic Technosols (Chromic, Colluvic, Eutric, Skeletic)													
Asp ₁	20-0	loose sandy quartz substance											
Asp ₂	20-0	dark cast iron - slag											
Asp ₂ k	0-30	5.26	4134.00	1443.99	108.41	8.35	4.95	3.35	8	25.7	100	0.23	38.4
AC _I	30-115	4.89	2489.79	1178.28	126.05	7.29	4.68	2.82	7.9	24.6	100	0.2	42.2
C _{II}	115-215	5.82	2854.41	987.06	200.32	6.15	8.05	2.55	7.2	24.1	94.6	0.13	19.1
Profile 13c Rhodic Eutric Cambisols (Clayic)													
A	0-32	3.72	894.48	811.88	24.63	6.94	3.56	2.36	7.8	33.1	100	0.81	60.8
AB	32-67								7.7	30.3	100	0.89	70.5
B ₁ w	67-116	3.88	1037.50	1502.27	36.36	13.50	3.13	5.03	7.8	32.5	100	0.63	73.7
B ₂ w	116-151								7.8	33	100	0.66	67.4
B ₃	151-185								7.8	35.1	100	0.92	70.5
B _C k	185-220	4.04	681.73	1652.07	50.64	14.25	5.43	7.03	8	31.4	100	0.28	55.7
C	220-260								8	31.8	100	0.3	49.8

Table 3. Concentration coefficients (CC) of the investigated elements, calculated as the ratio between the values in each of the horizons to the values in the lowest horizon of the profile.

CC	Te	Sb	Se	As
Prof. 3				
Asp ₂ k	0.72	2.12	0.74	0.71
B _I	0.88	0.93	0.91	1.24
1C	0.83	0.98	0.74	0.57
2Cg	1.00	1.00	1.00	1.00
Prof. 6				
Asp ₂ k	0.95	0.71	1.00	0.42
aC _f	1.13	1.03	0.98	0.79
C _{II}	0.96	0.87	0.96	0.67
C _{III} g	1.00	1.00	1.00	1.00
Prof. 7				
Ak	1.27	1.00	1.00	0.86
Bw(g)	0.42	1.10	0.71	0.72
C	1.00	1.00	1.00	1.00
Prof. 8				
AC _I g	2.41	1.55	1.86	2.43
AC _{III}	0.94	1.53	1.12	1.75
AC _{IV} g	1.00	1.00	1.00	1.00
Prof. 11				
Asp ₃ k	1.32	0.61	1.36	0.54
AC _I	1.11	0.58	1.19	0.63
C _{II}	1.00	1.00	1.00	1.00
Prof. 13c				
A	0.34	0.66	0.49	0.49
B _I w	0.72	0.58	0.95	0.72
BC	1.00	1.00	1.00	1.00

Another factor for the reduced mobility of Sb is the high content of As in the soil, which plays a limiting role at 60 - 230 µg / g As (Kabata-Pendias, 2011), and in the considered profile the values for arsenic are in the range 137 - 334 µg / g. The mechanism of upward movement of arsenic, antimony, selenium and tellurium, which in acidic environment are strongly adsorbed by soil colloids as negatively charged oxygen radicals (Sadiq, 1995, Denys, 2009, Missen, 2020, Cuvardic, 2003, Plant et al., 2003) is debatable. The measured acidity of pH 3.8 creates conditions for the destruction of soil colloids, which in the season of wetting, attracting with them the adsorbed ions rise and accumulate in the surface horizon. Confirmation of this thesis is the accumulation of physical clay in this horizon, which is more than the one below (Table 2), as well as the presence of pyrite and manganese stains (Stoykova and Teoharov, 2021).

The gravelly-sandy composition of the soil-forming sediments and the primitive structure of the polluted Regosols presented in profile 8 are a prerequisite for facilitating the rise of seasonal groundwater at the foot of the mountain slope and thus covering the entire soil profile from glaciation processes. On the same soil-forming materials in the near profile 7 a cambic soil-forming process takes place, which leads to a concentration of antimony only

in the cambic partial carbon horizon (CC = 1.1), again as a manifestation of its metallic properties, in association with iron, which is also maximum there (Table 2, Table 3, Figure 1).

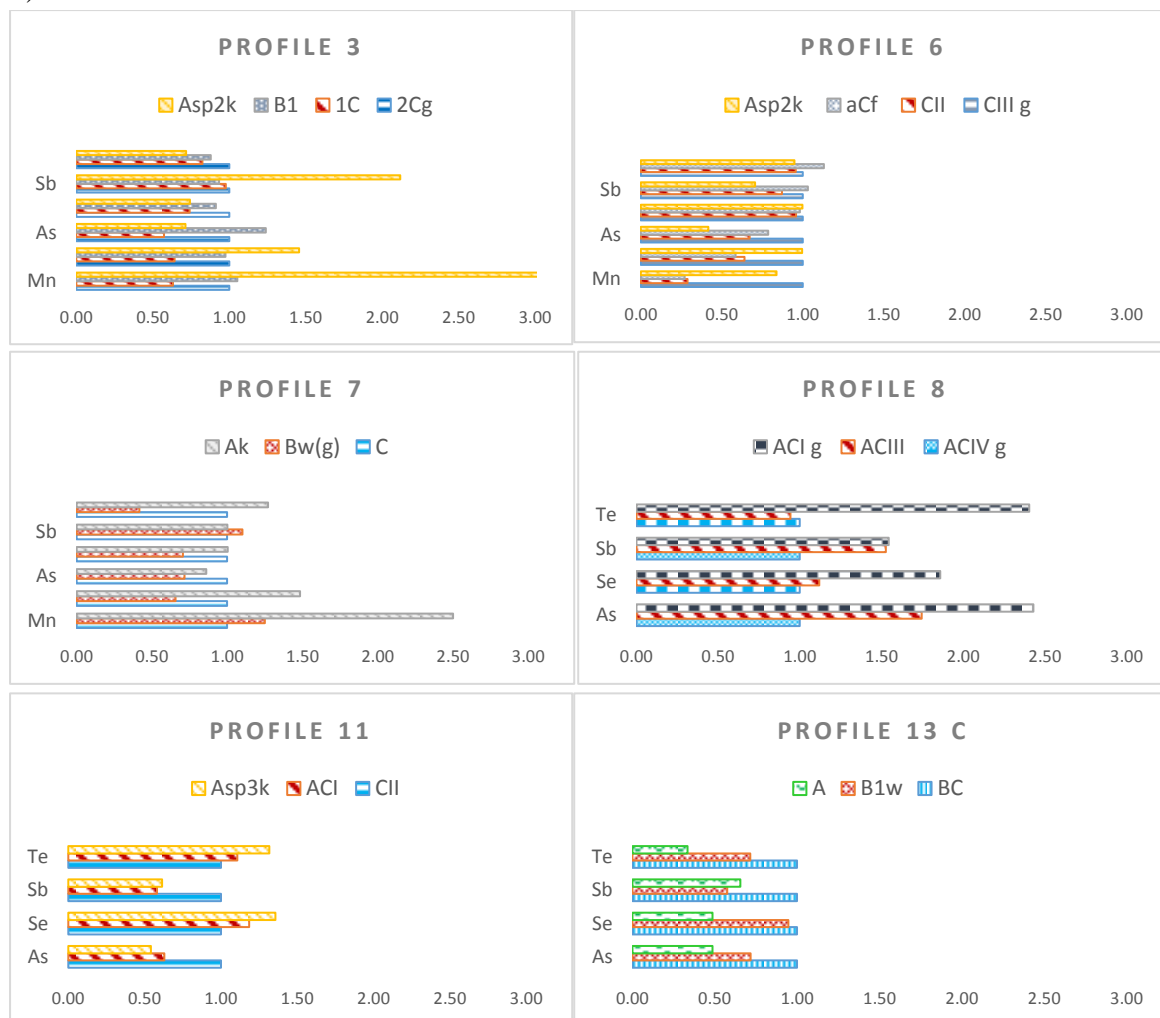


Figure 1. Bar charts of the Concentration coefficients (CC) of Te, Sb, Se and As in this study.

A general trend is shown by the four elements in their redistribution in Rhodic Cambisol, presented in the uncontaminated control profile 13c, as the concentration coefficients (CC) indicate their downward movement along the profile and their secondary accumulation in the B_{ck} horizon. Their downward movement is facilitated by the alkaline soil reaction (avg. pH 7.8), in which negatively charged oxygen radicals of metalloids are more mobile (Sadiq, 1995, Denys, 2009, Missen, 2020, Cuvardic, 2003, Plant et al. 2003). In the surface A-horizon their concentration is the lowest, with coefficients CC_{As} = 0.49, CC_{Se} = 0.49, CFS_b = 0.66, CCT_e = 0.34. Antimony is again an exception, as it relatively accumulates in the A horizon, relative to the intermediate B_{1w} horizon (CC = 0.58). This pronounced general tendency to impoverish the upper soil horizons in the unpolluted profile is in contrast to the erratic distribution of the four elements in the technogenic contaminated profiles (Figure 1). Technogenesis has influenced in such a way that in all contaminated profiles no microorganisms were identified, which are known to be an important factor in the processes of conversion of metalloids in the soil (Fatoki, 1997, Kabata-Pendias, 2011).

Microorganisms are known - fungi and bacteria, that biologically transform metalloids through reactions such as oxidation, reduction and methylation, leading to the formation of soluble or volatile organic compounds (Fatoki, 1997, Plant et al., 2003, Bentley and Chasteen, 2002). Methylation is also known to be a common mechanism by which cells metabolize metalloids and is key to the synthesis of volatile compounds leading to depletion of soil elements (Fatoki, 1997, Doran and Alexander, 1977, Missen, 2002, Bentley and Chasteen, 2002, Denys, 2009). In this sense, it could be reasonably argued that soil microorganisms, in the control example, but in the whole study, through their absence or presence are a leading factor in the distribution of arsenic, selenium, antimony and tellurium in soil profiles. Possible future remediation activities could be based on the pronounced biological sensitivity of these elements.

In profile 3 (Technosols, cambic), contaminated with agglomeration dust, rich in heavy metals in the form of technogenic salts (sulfates and carbonates) and Fe-Mn oxides and hydroxides and pH 8.4, only antimony has a CC above 1, i.e. it accumulates relatively in the surface horizon, and this is its highest concentration coefficient (CC) for all profiles – 2.12. Under these conditions, antimony is a companion of Mn, Fe, Pb, Mo, Cu and others technogenic pollutants (Stoykova, 2021), attached to Fe-Mn oxide and hydroxide structures, exhibiting their pronounced metallic properties, compared to other elements (Stefanova, 2005, Denys, 2009).

Table 4. Correlation coefficients (*r*) between test elements, reference macroelements and soil fractions.

	Fe	Mn	S	As	Se	Sb	Te	coarse and medium sand	fine sand	silt	clay
Fe	1	0.56	0.48	0.12	-0.09	0.85	-0.04	0.29	-0.40	-0.36	-0.42
Mn		1.00	0.70	0.56	0.10	0.62	0.19	0.57	-0.28	-0.49	-0.63
S			1.00	0.20	0.61	0.46	0.65	0.45	-0.18	-0.30	-0.48
As				1.00	0.10	0.42	0.09	0.53	-0.21	-0.18	-0.56
Se					1.00	0.03	0.92	0.09	0.02	0.06	-0.09
Sb						1.00	0.14	0.53	-0.15	-0.46	-0.72
Te							1.00	0.24	0.06	-0.11	-0.21

All the presented features are reflected in the derived correlation coefficients between the discussed p-elements and some benchmark macroelements - iron, manganese and sulfur. Confirmation of the strong attachment of antimony to iron and manganese are the calculated high values of the correlation coefficient - $r(\text{Sb-Fe}) = 0.85$, $r(\text{Sb-Mn}) = 0.62$ (Table 4). Man-made pollution with agglomeration dust also has a share in the formed large positive dependence with iron. Statistically significant, but weaker, is the relationship between arsenic and manganese ($r(\text{As-Mn}) = 0.56$). This dependence, as well as the Sb-Mn correlation, are a reflection of the influence of coarse-grained soil-forming materials on polluted Regosols containing ore. The same is reflected in the statistically significant positive indicators for the relationship between the three elements (Mn, As, Sb) and the large soil fraction. The highest calculated correlation coefficient is between selenium and tellurium - $r(\text{Se-Te}) = 0.92$. This indicator, together with statistically significant values for a positive correlation between the

two elements and sulfur, illustrates the primary influence of the halogen geochemical nature of these elements, as well as the influence of proluvial soil-forming materials rich in syenite and ongoing overwetting processes. Arsenic and antimony are also mobilized in these processes, but, although positive, their indicators for correlation with sulfur are not statistically significant.

Conclusion

After interpreting analytical data from 20 soil samples from Regosols and Cambisols, modified in Technosols, extremely high values for arsenic, antimony, selenium and tellurium content were determined compared to selected reference values - Te (56x) >> As (25x) > Se (24x) >> Sb (10x). The determined average contents are (in $\mu\text{g} / \text{g}$) As – 170,66 ($409.34 \div 24.63$); Se – 10.56 ($14.25 \div 6.15$); Sb – 6.66 ($13.93 \div 3.13$) and Te – 4.49 ($7.03 \div 2.14$). It was specified that the increased contents in these soils are the result of inheritance from proluvial soil-forming rocks, fed by two provinces - with predominant syenite or mineral-rich composition, and soil-forming and technogenic processes are subordinate. The natural soil-forming factors that affect the distribution of these related elements are the overwetting and the state of the soil microbiome. Contamination with agglomeration dust is the cause of antimony accumulation in the spolic horizon. Antimony, the only one, shows a deviation from the common geochemical trends for the four elements, as reflected in the statistically significant large positive dependence with iron - $r(\text{Sb-Fe}) = 0,85$. The determined very high natural content of the metalloid arsenic in the studied soils, including the arable ones, compared to the normatively determined maximum values in Bulgaria, is of public importance. The content of arsenic in Technosols is on average about 4 times above the maximum permissible concentration of metalloid in industrial soils ($40 \mu\text{g} / \text{g}$), and the arsenic in the control profile exceeds 1.5 times the established norm for the maximum permissible concentration in arable land ($25 \mu\text{g} / \text{g}$). Due to the high biological sensitivity of the four elements, possible future remediation activities could be based on microbiological and organic treatment in situ, following the necessary preliminary laboratory experiments.

References

- Angelov, V., M. Antonov, S. Gerdjikov, P. Petrov, S. Tanatsiev, H. Kiselinov, R. Marinova, V. Valev. (2008). *Geological map of Bulgaria M 1:50000*, m. pp. K-34-48-B (Elin Pelin). Research Institute of Geology and Geophysics JSC, MGU “St. Ivan Rilski”, S. (in Bulgarian)
- Bentley, R., Chasteen, T. G. (2002). Microbial Methylation of Metalloids: Arsenic, Antimony, and Bismuth. *Microbiology and Molecular Biology Reviews*, 66 (2), 250–271.
- Čuvarđić, M. (2003). Selenium in soil. *Proc. Nat. Sci. Matica Srpska Novi Sad*, 104: 23-37.
- Denys, S., Tack, K., Caboche, J., Delalain, P. (2009). Bioaccessibility, solid phase distribution, and speciation of Sb in soils and in digestive fluids. *Chemosphere*, 74(5), 711-716.
- Doran, J. W., Alexander, M. (1977). Microbial Formation of Volatile Selenium Compounds in Soil. *Soil Science Society of America Journal*, 41 (1), 70 p.
- Dyulgerov M. (2005). Potassium Alkaline Magmatism from Stara Planina, Bulgaria: Petrological study of Buhovo-Seslavtsi, Svidnia and Shipka plutons, Autoreph. Sofia University, University of Paris XI, Sofia, 35 p. (in Bulgarian)

Faitondjiev, L., L. Stanislavova, H. Thculdjian, B. Georgiev. (2000). Changes in the soils of the Kremikotzi Region. *Soil Sci. Agrochemistry and Ecology*, Sofia, 4, 3-10. (in Bulgarian)

Fatoki, O. S. (1997). Biomethylation in the natural environment: A review. *South African Journal of Science* 93, 366–370

Fersman, A.E. (1953). *Selected works*, vol. II. M., USSR Academy of Sciences, 768 p. (in Russian)

IUSS Working Group WRB. (2015). World Reference Base for Soil Resources 2014, update 2015, International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome, 192 p.

Kabata-Pendias A. (2011). Trace elements in soils and plants - 4th edition, Includes bibliographical references and index. CRC Press, NW, 534 p.

Kalaydzhiev, S. (1993). Structural control of uranium deposits in the area of the Iskar Gorge. – *Journal of Bulg. geol. Soc.* 54, 1, 13-20.

Kostov, I. (1993). Mineralogy. *Technique*, S., 734 p. (in Bulgarian)

Missen, O. P., Ram, R., Mills, S. J., Etschmann, B., Reith, F., Shuster, J., Smith, D. J., & Brugger, J. (2020). Love is in the Earth: A review of tellurium (bio)geochemistry in surface environments. *Earth-Science Reviews*, 204, [103150]. DOI: [/10.1016/j.earscirev.2020.103150](https://doi.org/10.1016/j.earscirev.2020.103150)

Plant, J. A., D. G. Kinniburgh, P. L. Smedley, F. M. Fordyce and B. A. Klinck. (2003). Arsenic and Selenium, *Volume 9 In: Treatise on Geochemistry*. Elsevier Ltd., 17–66

Regulation №3 of the MOEW on the standards for permissible content of harmful substances in soils. State Gazette, No. 71/01. August 2008. (in Bulgarian)

Rollinson, H. (1993). Using geochemical data: evaluation, presentation, interpretation. - Longman, 392 p.

Sadiq, M. (1995). Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. WRED, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, SA, 20 p.

Schulin, R., F. Curchod, M. Mondeshka, A. Daskalova, A. Keller. (2007). Heavy metal contamination along a soil transect in the vicinity of the iron smelter of Kremikotzi (Bulgaria). - *Geoderma*, 140, 52-61.

Stefanova, M.T. (2005). Fundamentals of geochemistry. SU "St. Kent Ohridski ", Sofia, 368 p. (in Bulgarian)

Stoykova, M. (2021). Characteristics of soils with geochemical and technogenic loading, formed on old Quaternary sediments. Abstract of the Ph. D. Thesis, IPAZR "N. Poushkarov", 32 p. (in Bulgarian)

Stoykova, M., M. Teoharov. (2021). Mineral composition of technogenic soils from the territory of the former metallurgical plant "Kremikotzi". Proceedings of the National Committee "Ecology and Agrotechnology - Basic Science and Practical Implementation", Volume 2, ISSN 2683-0663, 373 - 379. (in Bulgarian)

Teoharov, M. et al. (2019). Genetic and applied classifications of soils and lands in Bulgaria. Bulgarian Soil Science Society, Sofia, Avangard, 212 p. (in Bulgarian)



Erodibility Status of Some Soils in Akoko-Edo Local Government Area of Edo State, Nigeria.

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Abstract

Due to the detrimental effect of water erosion, erosion data must be gathered for sustenance of soil structure and utilization. The aim of the study was to determine the erodibility status of the some soils in Akoko-Edo Local Government Area of Edo state, Nigeria. Soil samples were taken from representative pedons dug from the three communities namely Ikpeshi, Unem-Nekhwa and Ososo. The samples were subjected to routine analysis and results were used to calculate the erodibility indices of Clay Dispersion Ration (CDR), Clay Disperion Index (CDI), Clay Flocculation Index (CFI) and Bouyoucous Erodibility Index (EI_{ROM}). The data derived were subjected to statistical analysis, to determine mean separation at 5% probability, coefficient of variation and standard error. The results showed that the soils were dominated by the sand fraction, mainly sandy loam with clay increment down the horizons becoming loamy sand and sandy clay loam. Soil pH ranged from an average of 5.36 – 5.62 across the pedons. Electrical Conductivity (EC) mean across the pedons ranged from 23.88 $\mu\text{S}/\text{cm}$ (0.02388 dS/m) - 36.11 $\mu\text{S}/\text{cm}$ (0.0361 dS/m) which posed no salinity threat. Organic matter was low with average of 9.28 – 14.85 g/kg across the pedons. Across the horizons, the CDR ranged from 53.7 - 62.3%, CDI (42.5 - 59.2%), CFI (34.52 - 43.1%) and EI_{ROM} (1.92 - 3.93). Clay had highly significant negative correlation ($r = -0.7235$) with CDI and EI_{ROM} ($r = -0.9730$). Sand had positive correlation with CDI ($r = 0.7597$) and EI_{ROM} ($r = 0.9130$). CDR also had a positive correlation ($r = 0.8306$) with CDI. CDI had a positive correlation ($r = 0.6945$) with EI_{ROM} . Variation for all index was low, ranging from 0.1-3. The result shows that the soils are erodible and sustainable and conservational agriculture practice should be carried out.

Keywords: Akoko-Edo, erodibility, Edo state, Nigeria, status

Introduction

The need to gather information on soil conditions cannot be overemphasized, as there is an up rise in the use of land indiscriminately and also misappropriate land use systems. Soil erosion is dependent on erosivity by rainfall and the erodibility which is the resistance of the soil to destruction by external forces. The erodibility of any soils depends on the soil type, texture, level of aggregation, infiltration rate etc. Areas like Ogbogoro community in Bayelsa

State, devoid of soil erodibility data are currently in distress, as the area is ravaged by severe erosion.

As stated by Nyakatawa *et al.* (2001), soil erosion is a major environmental problem worldwide.

More than 56 % of land degradation is caused by soil erosion, raising a global concern on land productivity (Elirehema, 2001). Water erosion conveys soils, its nutrients, pesticides and other harmful chemicals into nearby rivers, streams and eventually polluting groundwater. Eroded soils are deposited in water bodies leading to pollution and siltation, which causes reduction of water quantity, quality, siltation and drying up of water bodies. Thus, aquatic life is threatened and eventually eliminated, while land productivity is negatively affected. Soil erosion is one of the most serious forms of land degradation in the world (Sohan and Lal, 2001).

Another problem associated with erosion include economic, political, social and environmental downturn which result from direct or indirect damages to the soil; which does not only cause severe land degradation and low soil productivity but also threatens the general health of society, sustainable development and habitation of rural areas, with the dwellers in particular (Tang, 2004; Zheng *et al.*, 2004; Jing *et al.*, 2005).

Consequently, erodibility data must be provided, in order to enable agriculturists, engineers and other land users to identify areas prone to erosion. This will enable them practice sustainable agriculture, and suitable land use systems, which will help control the soil erosion and its hazards. Hence, the study was undertaken to assess the current erodibility status of some soils in Akoko-Edo Local Government Area of Edo State, Nigeria.

Materials and Methods

Study Area

The study sites are situated in Akoko-Edo local government area of Edo state, which has Ogori /Mangogo, Okehi, Adavi and Okene local government areas all in Kogi state to the North; Akoko South East, Akoko North East and Ose local government areas in Ondo state to the West; to the South: Owan East and Etsako west; and to the East with Etsako East.. It occupies an area of 1,371 km² (137,100 hectares) and lies between longitude 6° 06' 0" E and latitude 7° 17' 0" N.

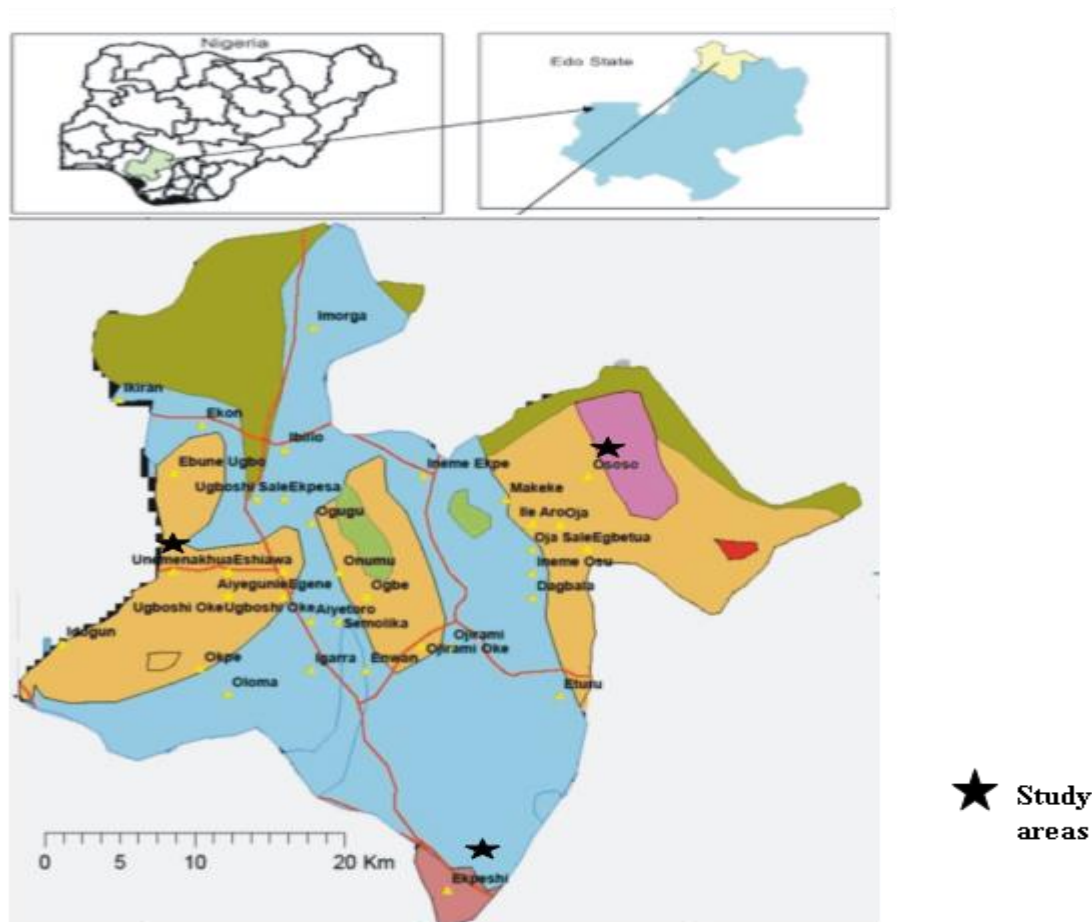
The three areas (Ikpeshe - N 07.18674°, E 006.15456°, Unem Nekhua - N 07.33174° E 006.08360° and Ososo - N 07.40648°, E 006.25318°) were considered.

Climate

Akoko Edo Local Government area is characterized by tropical climate with an annual average rainfall amount of 1200 - 1500 mm, mean annual temperatures range of 27° C to 32° C and mean annual relative humidity ranging from 30.5 % to 94.0 %. The study area is characterized by two distinct seasons: the wet and the dry. The rainfall is at its climax in July and August with a short break in mid-August. The dry season begins early November and ends by March (Olowojoba *et al.*, 2016).

Geology

The area lies within the basement complex formation, which consists of various minerals like shale, coarse grained granite and granite gneiss etc with some outcrops visible around the entire local government area. Physiographically, the project area can be described as



Land use

Vegetation

Soil sampling

Three profile pits were dug, representing three mapping units/area including: Ikpeshi, Unem-Nekhwa and Ososo. Soil samples were taken from each distinctive horizons of the soil

profiles according to Schoeneberger *et al.* (2012) guidelines. A total of seventeen (17) soil samples were acquired from the three pedons, and were subjected to routine and special laboratory analysis.

Laboratory analysis

Particle size distribution was determined by Bouyoucos hydrometer method (Gee and Or, 2002). Soil pH and Electrical conductivity was determined electrometrically using the glass electrode pH and EC meter in a solid-liquid (water) ratio of 1:2.5 (Hendershot et al., 1993). Organic carbons were determined using Walkley-Black wet oxidation methods (Walkley and Black, 1934). The organic matters were computed by multiplying the value of the organic carbon by a value of 2.0 by Douglas W. Pribyl (2010). Exchangeable bases were determined by the neutral ammonium acetate procedure buffered at pH 7.0 (Thomas, 1982). Exchangeable acidity was determined by a method described by McLean (1982). Soil bulk density was determined by the core method (Grossman and Reinsch, 2002). Total porosity (Po) was obtained from bulk density (ρ_p) values with an assumed particle density value of (ρ_s) 2.65 gcm⁻³ as follows, Porosity (Po) = $100 - (\rho_p/\rho_s) \times 100/1$.

Erodibility index

The new and advanced Bouyoucos (1962) erodibility index will be used to analyze the erodibility status

$$EI_{ROM} = \frac{\% SAND + \% SILT}{2 (\% CLAY)}$$

Table 1. 'ROM' Scale with regards to soil erodibility category (Roslan & Mazidah, 2002).

ROM SCALE	SOIL ERODIBILITY CATEGORY
< 1.5	Low
1.5 ~ 4.0	Moderate
4.0 ~ 8.0	High
8.0 ~ 12.0	Very high
> 12.0	Critical

The clay-dispersion indices were calculated as follows;

Clay dispersion ratio (CDR) = $\{(\% \text{ silt} + \text{clay (H}_2\text{O)}) / \{ \% \text{ silt} + \text{clay (Calgon)}\} \times 100$

Clay dispersion index (CDI) = $\{[\% \text{ clay (H}_2\text{O)}] / [\% \text{ clay (Calgon)}]\} \times 100$

Clay flocculation index (CFI) = $[\% \text{ clay (Calgon)}] - [\% \text{ clay (H}_2\text{O)}] / [\% \text{ clay (Calgon)}] \times 100$

The higher the CDR and CDI the more the ability of the soil to disperse while the higher the CFI, the better aggregated the soil. Clay dispersion ratio was used to determine the erodibility of the soils in which greater than 15% are erodible and less than 15 % are not erodible (Middleton, 1930)

Statistical Analyses

The data generated were evaluated using the Coefficient of variations as designated by Wilding *et al.* (1994) to determine the gradation of disparity among horizons of each pedon. GenStat 12th Edition application were summarized using mean, mean separation (Duncan Multiple Range Test) at 5% level of probability. The correlation matrix was used to determine the association between some selected properties of the soil.

Results and Discussions

Soil Particle Distribution

Table 2. Some soil physical properties of the study area

Horizons	Depth (cm)	Clay	Silt	Sand	Textural Class	Bulk Density g/cm ³	porosity %
Ikpeshi Soils N 07.18674°, E 006.15456°							
Ap	0 - 24	92.70 ^e	100.00 ^a	807.30 ^b	Loamy sand	1.457 ^a	44.91 ^d
A	24 - 41	104.30 ^d	75.0 ^b	820.70 ^a	Loamy sand	1.743 ^c	34.34 ^b
Bt1	41 - 76	225.0 ^c	58.00 ^e	717.00 ^c	Sandy clay loam	1.633 ^b	38.49 ^c
Bt2	76 - 111	248.33 ^a	60.67 ^c	691.00 ^e	Sandy clay loam	1.787 ^d	32.45 ^a
Bt3	111 - 147	238.0 ^b	60.00 ^d	702.00 ^d	Sandy clay loam	1.743 ^c	34.34 ^b
Mean		181.66	70.73	747.6		1.6726	36.91
Unem-Nekhwa N 07.33174° E 006.08360							
A	0 - 14	98.00 ^e	65.00 ^b	837.00 ^c	Loamy sand	1.533 ^b	42.26 ^e
AB1	14 - 40	105.00 ^d	46.00 ^e	849.00 ^b	Loamy sand	1.453 ^a	45.28 ^f
AB2	40 - 64	108.70 ^c	69.30 ^a	822.00 ^d	Loamy sand	1.563 ^c	41.13 ^d
BA	64 - 82	90.00 ^f	41.00 ^f	869.00 ^a	Sand	1.587 ^d	39.67 ^c
Bt1h	82 - 118	135.00 ^b	56.00 ^c	809.00 ^e	Sandy loam	1.673 ^f	36.98 ^b
Bt2h	188 - 193	189.30 ^a	51.00 ^d	759.70 ^f	Sandy loam	1.653 ^e	34.67 ^a
Mean		121	54.71	824.28		1.577	39.998
Ososo soils N 07.40648°, E 006.25318°							
A	0 - 26	120.00 ^f	95.00 ^b	785.00 ^a	Sandy loam	1.283 ^a	51.73 ^e
Bw1	26 - 49	205.00 ^e	89.00 ^c	706.00 ^b	Sandy clay loam	1.567 ^c	39.62 ^b
Bw2	49 - 83	238.00 ^c	80.00 ^d	682.00 ^c	Sandy clay loam	1.683 ^d	36.63 ^a
Bw3	83 - 114	288.00 ^a	75.00 ^e	637.00 ^c	Sandy clay loam	1.587 ^c	40.33 ^c
Bw4	114 - 144	220.70 ^d	183.31 ^a	596.00 ^f	Sandy clay loam	1.607 ^c	39.25 ^b
Bw5	144 - 187	285.00 ^b	70.00 ^f	645.00 ^d	Sandy clay loam	1.423 ^b	46.25 ^d
Mean		226.11	98.71	675.16		1.525	42.3

Mean value(s) with the same letters(s) in the column are not significantly different from one another at 5% level of probability in each location.

The result from table 2 shows that sand fraction dominated all the horizons of the Ikpeshi soils, followed by clay, and then silt. The soils had a mean of 747.6 g/kg sand, 181.66 g/kg clay and 70.73 g/kg. The sand content reduced down the horizon while the clay fraction increased downwards. The soil texture was loamy sand at the first two horizons and sandy clay loam for the remaining three horizons. The sandy and coarse nature of Ikpeshi soils is greatly related to the parent material: basement complex formation, which consists of various minerals like shale, coarse grained granite and granite gneiss (Weil and Brady, 2016). The increase in clay down the horizon indicates the process of illuviation Niu *et al.* (2015). In Ikpeshi soils, the bulk density ranged from 1.457 – 1.787 g/cm³ with an average of 1.67

g/cm³. The bulk density of the Ikpeshi soil was high indicating compaction, in exception of the first horizon which had been ploughed. The bulk density values affected the porosity of the soils, the horizon with low bulk density had lower porosity of 44.91% while the highest bulk density of 1.787 g/cm³ registered a porosity of 32.45%; lower bulk density begot higher porosity while higher bulk density begot lower pore spaces.

Table 3. Selected Chemical Properties of the Pedons

Horizons	Depth (cm)	pH	EC	Org.C	Org.M	CEC	ECEC
			µS/cm	← g/kg →		← cMol/kg →	
Ikpeshi Soils							
N 07.18674°, E 006.15456°							
Ap	0 - 24	4.43 ^d	20.53 ^d	11.93 ^a	20.56 ^a	2.36 ^d	3.16 ^c
A	24 - 41	5.73 ^c	24.63 ^c	4.43 ^d	7.63 ^d	2.80 ^b	3.43 ^b
Bt1	41 - 76	6.10 ^a	52.80 ^a	10.90 ^b	18.79 ^b	2.44 ^d	2.84 ^e
Bt2	76 - 111	5.96 ^b	31.73 ^b	7.93 ^c	13.67 ^c	2.61 ^c	3.04 ^d
Bt3	111 - 147	5.90 ^b	24.70 ^c	7.90 ^d	13.61 ^c	3.00 ^a	3.60 ^a
	Mean	5.62	30.88	8.6	14.85	2.64	3.21
Unem-Nekhwa							
N 07.33174° E 006.08360							
A	0 - 14	4.80 ^e	17.20 ^e	2.50 ^e	4.31 ^e	2.22 ^b	3.03 ^c
AB1	14 - 40	5.60 ^c	39.3 ^a	6.30 ^c	10.86 ^c	2.44 ^b	3.24 ^a
AB2	40 - 64	5.20 ^d	20.30 ^d	6.20 ^d	10.68 ^d	2.32 ^b	2.92 ^e
BA	64 - 82	4.30 ^f	6.50 ^f	1.70 ^f	2.93 ^f	3.08 ^a	3.22 ^b
Bt1h	82 - 118	6.60 ^a	24.40 ^c	6.40 ^b	11.03 ^b	2.26 ^b	2.66 ^f
Bt2h	188 - 193	5.66 ^b	35.63 ^b	9.23 ^a	15.91 ^a	2.33 ^b	2.92 ^d
	Mean	5.36	23.88	5.38	9.28	2.44	3
Ososo soils							
N 07.40648°, E 006.25318°							
A	0 - 26	5.50 ^b	49.50 ^a	7.90 ^b	13.61 ^b	2.50 ^e	3.30 ^f
Bw1	26 - 49	5.50 ^b	40.10 ^b	8.00 ^a	13.79 ^a	3.16 ^b	3.96 ^a
Bw2	49 - 83	5.10 ^c	29.30 ^e	7.80 ^d	13.44 ^d	2.78 ^d	3.58 ^e
Bw3	83 - 114	5.60 ^a	37.40 ^c	6.90 ^e	11.89 ^e	3.34 ^a	3.94 ^b
Bw4	114 - 144	5.23 ^d	32.00 ^d	7.86 ^c	13.55 ^c	3.08 ^c	3.84 ^c
Bw5	144 - 187	5.30 ^d	28.40 ^f	6.40 ^f	11.03 ^f	3.08 ^c	3.68 ^d
	Mean	5.37	36.11	7.47	12.88	2.99	3.71

EC: Electrical Conductivity, OC-Organic Carbon, OM – Organic Matter, CEC- Cation Exchange Capacity, ECEC – Effective Cation Exchange Capacity

In Unem-Nekhwa soils, the sand fraction also dominated the horizons with an average of 824.28 g/kg, followed by clay with a mean of 121 g/kg and silt 54.71 g/kg. The texture ranged from loamy sand to sand to sandy loam indicating a reduction of the sand fraction and clay increment down the horizon. Illuviation also took place in the soils. The bulk density increased down the profile with an average of 1.577 g/cm³ and an average porosity of 39.99%

Ososo soils recorded the highest clay content with an average of 226.11 g/kg and lowest sand fraction of 675.16 g/kg, the soils were majorly sandy clay loam apart from the

first horizon. The soils had the lowest average bulk density of 1.53 g/cm^3 and highest porosity of 42.3%.

Some chemical properties of the study areas

Ikpeshi soils had a pH of 4.43 – 6.10 which is strongly acidic to slightly acidic. The high acidity could be linked to the leaching of basic cations caused by the high rainfall in the region Niu *et al.*, (2015). The electrical conductivity ranged from 20.53 – 52.80 $\mu\text{S/cm}$ with a mean of 30.88 $\mu\text{S/cm}$ (0.03088 dS/m). This value according to the Ganjegunte *et al.* (2018) places the soil less than four (<4), which is non saline, indicating that there is no obstruction to the soil structure and it poses no threat to seedlings and salt sensitive crops. Organic carbon and organic matter low to moderate with a range of 4.43 – 11.93 g/kg and 7.63 – 20.56 g/kg. The low effective cation exchange capacity ranged from 2.84 – 3.60. This concurred with the findings of Gaillyson and David (2013). The low CEC and ECEC indicated that the pedons have low activity clays and are highly weathered according to the finding of Soil Survey Staff (2014). The highly weathered soils are more susceptible to erosion due to the formation of coarse particle which encourages poor aggregation.

Unem-Nekhwa soils had pH with a mean of 5.36, EC of 23.88 $\mu\text{S/cm}$ (0.02388 dS/m), Organic Carbon and Organic matter of 5.38 and 9.28 g/kg, Cation Exchange Capacity and Effective Cation Exchange Capacity of 2.44 and 3 cMol/kg while Ososo soils recorded a mean pH of 5.37, EC of 36.11 $\mu\text{S/cm}$ (0.0361 dS/m), OC and OM of 7.47 and 12.88 g/kg; with CEC and ECEC of 2.99 and 3.71 cMol/kg. The interpretations for Unem-Nekhwa and Ososo were all similar to that of the Ikpeshi soils.

From the result in table 4, Ikpeshi soils had a Clay Dispersion Ratio (CDR) ranging from 44 – 67% with a mean of 53.5%. Variation and standard error amongst the generic horizons were low with 0.1 coefficient of variation (CV) with standard error (SE) of 0.0577. The Clay Dispersion Index (CDI) ranged from 40.4 – 52% with an average of 44.2; the coefficient of variation and standard error were 0.1 and 0.0577. The Clay Flocculation Index (CFI) ranged from 30.7 – 39.9% with a mean of 34.52, Coefficient of Variation of 0.2 and Standard error of 0.0577. The Bouyoucos Erodibility Index (EI_{ROM}) ranged from 1.52 – 4.88 with a mean of 2.80, CV of 0.9 and SE of 0.02633. The CDR, CDI, CFI and EI_{ROM} registered low variations amongst the different horizons.

The CDR of the Ikpeshi soils was far above 15% in all the horizons indicating that they are weak soil structure and are erodible. The CFI which is another factor used to determine the resistance of soils to dispersion, was also low indicating low resistance of the soils to external erodible forces. The CFI connotes the ability of the soils to aggregate; the Ikpeshi soils recorded low CFI, thus weak aggregation. The EI_{ROM} on the other hand ranged from high to moderate down the horizons.

The CDR in Unem-Nekhwa soils ranged from 50.5 – 77% with a mean of 62.3%, CDI (50 – 66.2%, mean – 59.2), CFI (33.5 – 40.89% with mean of 36.4) and EI_{ROM} had a range of 2.3 – 5.1 with a mean of 3.90. The coefficient of variation and standard error were 0.1 for CDR, CDI, CFI respectively, 1.5 for EI_{ROM} and 0.0473 for CDR, 0.0577 for CDI, 0.0410 for CFI, & 0.0577 for EI_{ROM} . The table 4 shows that CDR and CDI were above 15% indicating that the soils are erodible, also the CFI for the different horizons were low, showing weak aggregation. The EI_{ROM} indicated that the erodibility was high to moderate.

Table 4. Erodibility indices of the study areas

Horizons	Depth (cm)	CDR	CDI	CFI	EI _{ROM}
←———— % —————→					
Ikpeshi Soils					
N 07.18674°, E 006.15456°					
Ap	0 - 24	67 ^e	52 ^d	39.9 ^e	4.88 ^e
A	24 - 41	44 ^a	40.4 ^a	30.7 ^a	4.31 ^d
Bt1	41 - 76	57.4 ^d	45.8 ^c	35.7 ^d	1.72 ^c
Bt2	76 - 111	51.1 ^c	42.5 ^b	33.3 ^c	1.52 ^a
Bt3	111 - 147	49 ^b	40.3 ^a	33 ^b	1.6 ^b
	Mean	53.7	44.2	34.52	2.80
	CV	0.1	0.1	0.2	0.9
	SE	0.0577	0.0577	0.0577	0.02633
Unem-Nekhwa					
N 07.33174° E 006.08360					
A	0 - 14	77 ^f	66.2 ^f	34.01 ^b	4.6 ^e
AB1	14 - 40	50.52 ^a	50 ^a	40.89 ^f	4.3 ^d
AB2	40 - 64	56.8 ^b	55.1 ^b	39.02 ^e	4.1 ^c
BA	64 - 82	67.9 ^e	65.8 ^e	33.5 ^a	5.1 ^f
Bt1h	82 - 118	61.41 ^d	60.7 ^d	34.8 ^c	3.2 ^b
Bt2h	188 - 193	60 ^c	57.6 ^c	36 ^d	2.3 ^a
	Mean	62.3	59.2	36.4	3.93
	CV	0.1	0.1	0.1	1.5
	SE	0.0473	0.0577	0.0410	0.0577
Ososo soils					
N 07.40648°, E 006.25318°					
A	0 - 26	57 ^e	50.5 ^e	45.05 ^e	3.7 ^d
Bw1	26 - 49	56.2 ^d	46.9 ^d	42.6 ^d	1.9 ^c
Bw2	49 - 83	56 ^c	42.3 ^c	42 ^c	1.6 ^b
Bw3	83 - 114	56.01 ^c	40.8 ^b	41.7 ^b	1.2 ^a
Bw4	114 - 144	50.3 ^b	40.8 ^b	41.6 ^a	1.8 ^c
Bw5	144 - 187	49.3 ^a	33.7 ^a	45.8 ^f	1.3 ^a
	Mean	54.1	42.5	43.1	1.92
	CV	0.1	0.1	0.1	3.0
	SE	0.0528	0.0577	0.0528	0.0577
CV – Coefficient of Variation SE – Standard Error CDR – Clay Dispersion Ration					
EI _{ROM} - Bouyoucos Erodibility Index CDI – Clay Dispersion Index CFI – Clay Flocculation Index					

In Ososo soils, the CDR ranged from 49.3 – 57% with a mean of 54.1% , CV (0.1), and SE of 0.0528. The CDI was 33.7-50.5% with a mean of 42.5%, CV of 0.1 and SE of 0.0577. CFI ranged from 41.6 - 45.8% with a mean of 43.1%, CV of 0.1 and SE of 0.0528. EI_{ROM} ranged 1.3-3.7 with a mean value of 1.92, CV of 3.0 and SE of 0.0577. The data shows that, like the other soils, the Ososo soils are also erodible. Igwe and Udegbumam (2008), also reported that DR, CDI, and CFI were high when compared to the soils of Southern Nigeria. The result when correlated to the findings of Oguike and Mbagwu (2009) in soils of Southern Nigeria shows that DR and CDI were high while CFI was low.

Table 5 shows the correlation matrix between some erodibility indices and some selected soil physical properties. Clay had highly significant negative correlation ($r = -0.7235$) with CDI and EI_{ROM} ($r = -0.9730$). Sand had positive correlation with CDI ($r = 0.7597$) and EI_{ROM} ($r = 0.9130$). CDR also had a positive correlation ($r = 0.8306$) with CDI. CDI had a positive correlation ($r = 0.6945$) with EI_{ROM} .

Table 5. Correlation matrix of erodibility indices and some selected soil physical properties

	CLAY ←	SILT g/kg	SAND →	CDR ←	CDI %	CFI →	EI_{ROM}
CLAY	1						
SILT	0.1507	1					
SAND	-0.9227**	-0.5199	1				
CDR	-0.4585	-0.1878	0.4664	1			
CDI	-0.7235**	-0.3490	0.7597**	0.8306**	1		
CFI	0.2917	0.4248	-0.4167	-0.1374	-0.3473	1	
EI_{ROM}	-0.9730**	-0.1858	0.9130**	0.4918	0.6945**	-0.2713	1

Conclusion

The results of the study areas show that the soils were dominated by the sand fraction which could be attributed to the parent material, the pH was acidic to slightly acidic; the soil of the three areas recorded low electrical conductivity indicated no threat of salinity and obstruction. The organic matter and cation exchange capacity was also low. The erodibility indices used stated that the soils are erodible. This could be related to the low organic matter content and lower clay fraction, which could serve as soil binding agents and improve soil structure and aggregation. The destructive power of erosion on agriculture can never be overemphasized, hence conservation methods such as cover cropping, contour cropping, slope terracing, and conservational tillage methods etc should be practiced to control and limit soil erosion.

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References

- Bouyocous G.J. (1962). Hydrometer method improved for making particle size analysis of soil. *Agr. J.* 54: 3.
- Douglas W. P. (2010). A Critical review of the conventional SOC to SOM conversion factor. *Geoderma*, Vol. 156, Pp. 75- 83.
- Elirehema, Y.S. (2001). Soil Water Erosion Modeling in Selected Watersheds in Southern Spain. IFA, ITC, Enschede.
- Gaillyson, Y.J. and David, O.O. (2013). Soil profile characteristics as affected by land use systems in the Southeastern Adamawa state, Nigeria. *Journal of Agriculture and Veterinary Science*, Vol. 6 (4) 04 - 11.
- Ganjegunte, G. K, Clark J. A., Parajulee M. N., Enciso, J. and Kumar, S. (2018). Salinity management in pima cotton fields using sulfur burner. *Agrosystems, Geosciences and Environment*, 1: 180006.

Gee, G.W., Or, G. (2002). Particle size, In: Dane J.H. & Topp, G.C. (eds). *Methods of Soil analysis. Part 4 Physical methods*. Soil Science Society of America Madison, WI, Book Series No. 5 ASA and SSA 255 – 293.

Grossman, R.B., Reinsch, T.G. (2002). Bulk Density and linear extensibility. In: Dane, J.H., and Top G.C. (Eds). *Methods of soil analysis* (part 4, physical methods). (pp. 201-228). Soil Science Society of America. Book series no. 5. ASA and SSA Madison, WI, USA.

Hendershort, W.H., Lalande, H., & Duquette, M. (1993). Soil reaction and exchangeable acidity. In: Carter M.R. (ed), *Soil Sampling and methods of soil analysis*. (pp. 141-145). Canadian Society of Soil Science, Lewis Publishers, London.

Igwe, C. A., Udegbumam, O. N. (2008). Soil properties influencing water-dispersible clay and silt in an Ultisols in Southern Nigeria. *International Agrophysics*, 22, 319 – 325.

Jing, K., Wang, W.Z. and Zheng, F.L. (2005). Soil erosion and environment in Beijing, China. Science Press.

McLean, E. O. (1982). Aluminum. In: C.A. Black (Ed.). *Methods of soil analysis*. Agron. No. 9. Part II. *Am. Soc. Agron*, Madison, Wisconsin USA.

Middleton, H. E. (1930). Properties of soils which influence soil erosion. *Tech. Bull.* no. 178. Washington, DC: USDA

Niu, D.F., Li, B.S., Wang, F.N., Wen, X.H., Ma, J.L. Shu, P.X., (2015) Climate changes indicated by the clay minerals: A case of the Dishagouwan section on the south eastern margin of the Mu Us Desert. *Journal of Fuzhou University* (National Science Education) 43: 345–351.

Nyakatawa, E.Z., Reddy, K.C., Lemunyon, J.L. (2001). Predicting soil erosion in conservation tillage cotton production systems using the revised universal soil loss equation (RUSLE). *Soil and Tillage Research*, 57 (4), 213-224.

Oguike, P. C., Mbagwu, J. S. C. (2009). Variations in some physical properties and organic matter content of soils of coastal plain sand under different land use types. *World Journal of Agricultural Sciences*, 5 (1): 63 – 69.

Olowojoba S.O., Kappo A.A., Ogbole J.O., Alaga A.T., Mohammed S.O., Eguaroje E.O. (2016). Land Suitability and Evaluation for the Production of Cassava in Akoko-Edo L.G.A. of Edo State using Geo-Technology Techniques. *Greener Journal of Agricultural Sciences*, 6(2): 059-068, <http://doi.org/10.15580/GJAS.2016.2.011416008>

Schoeneberger, P.J., Wysocki D.A., Benham E.C., (2012). Field book for describing and sampling soils, Version 3.0. Natural Resources Conservation Service, National Soil Survey Center, Lincoln, NE.

Sohan, W., Lal, S. (2001). Extraction of parameters and modeling soil erosion using GIS in an arid environment. Center for Remote Imaging, *Sensing and Processing*.

Soil Survey Staff. (2014). Soil Survey Field and Laboratory Methods Manual. Soil Survey Investigations Report No. 51, Version 2.0. R. Burt and Soil Survey Staff (ed.). U.S. Department of Agriculture, Natural Resources Conservation Service.

Tang, K.L. (Ed) (2004). Soil and Conservation in Beijing, China. *Science Press*.

Thomas, G. W. (1982). Exchangeable Cations. In: A. L. Page; R. H. Miller and D. R. Keeney (eds.). *Methods of Soil Analysis, Part 2, Chemical and Microbiological properties*. Madison, Wisconsin. Pp. 159 – 164.

Walkley, A., Black, I.A. (1934). An examination of the different methods for determining soil organic matter and the proposed modification of the chromic acid wet titration method. *Soil Science of America Journal*. 37: 29 – 38.

Weil, R.R and Brady, N.C (2016). The Nature and Properties of Soils. (15th Ed) *Pearson Education*. ISBN: 978- 0133254488.

Wilding, L.P., Bouma, J. and Boss, D.W. (1994). Impact of spatial variability on interpretative modeling. In: *Quantitative modeling of soil forming processes*. Bryant, R.B. and Arnold, R.W. SSSA. Special Publication. No.39: 61.

Zheng, F., Stephen, D.M., Huang, C., Tanaka, D.L., Darboux, F., Liebig, M.A, Halvorson, A.D. (2004). Runoff, soil erosion and erodibility of Conservation Reserve Program land under crop and hay production. *Soil Science Society of American Journal*, Vol. 68 (4): 1332 – 1341.



Changes in the Properties of Luvisols, Planosols and Fluvisols Under the Influence of Agroproduction Activity from the Region of Sofia District

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Abstract

The soils from the Dolna Banya valley of Sofia district are formed under forest meadow, bush and tree vegetation. It has influenced their texture, natural fertility and the reaction of the soil solution. As they are located in a semi-mountainous terrain, surface horizons are subject to erosion processes and podzolization.

The aim of the research is to establish the changes in the profile of Rhodic Luvisols which occurred as a result of natural influences and the type of production activity on them.

The research has found that for a long time there have been changes in the surface soil horizons of all studied differences of Rhodic Luvisols. The process of podzolization continues to develop and there is an increase in the content of silt in the horizons below the humus horizon. In the case of Fluvisols, an increase in the fraction of coarse and fine sand is reported. In the case of moderately eroded Planosols land use has an impact on the soil texture. In the deeper horizons, when planted with raspberries, the content of silt and physical clay increases compared to the same soil difference in the area with the application of three-field crop rotation, compacted with cereals using a shallow mouldboard ploughing.

Keywords: Fluvisols, Luvisols, Planosols, Sofia district, process of pseudopodzolization, soil texture, three-field crop rotation

Introduction

From the fact that the properties of the soils and the degree of their fertility depend a lot on the type and age of the parent rocks, on the relief, exposure, latitude and altitude, as well as on the climatic conditions that activate or suppress more or less biological activity, the state and biological potential of soil differences are determined (Teoharov 2004; Blum, 2007; Kinoshita et al., 2017). This feature of the soil formation process is an objective basis for the action of the third law of agriculture: "for the unity and interdependence of growth and development of plant associations and their habitat" from which arises the objective need for an ecological approach in organizing and managing production in crop production (Krastanov, 2006; Ugarte et al., 2016).

The soils from the Dolna Banya valley are formed under forest meadow, bush and tree vegetation, which has affected their texture, natural fertility and the reaction of the soil

solution (Koynov et al., 1972; Penkov et al., 1985; Ninov et al., 1985; Boneva et al., 2005; IUSS Working Group, 2015; Teoharov et al., 2019).

As they are located on a semi-mountainous terrain characterized by rough terrain with ravines and gullies that have slope 8-10° and the soil surface horizons are subject to erosion processes and pseudopodzolization. The climate is transition continental region of the European continental climate and is temperate continental influenced by the river valley of Maritsa river and its tributaries (Boneva et al., 2005; Ninov, 2007).

Economic activity in the past was determined by the cultivation of cereals, fiber crops, potatoes and mainly berry crops, natural and artificial pastures and meadows.

The aim of the research is to establish the changes in the profiles of Luvisols, Fluvisols and Planosols which occurred as a result of natural influences and the type of land use on them.

Materials and Methods

The subject of the study are the following differences of soils:

Rhodic Luvisols, slightly eroded.

They are distributed in the form of individual spots in the southeastern and northeastern part of the land. They occupy an area of 3875 da - which represents 2.39% of the total area. They are formed on non-carbonate weathering products under the influence of forest vegetation. As a result of the recent slight erosion, part of the light surface horizon has been removed, due to which the profile is somewhat shortened. The profile is clearly differentiated. Most of the area of the considered soil differences is included in the arable fund of the farm units. An idea of the morphological structure of these soils is given by the description of profiles made one kilometer northeast of the village of Pchelin (Yolevski, M. et al. 1974).

A₁B fallow land 0- 20 yellowish-brown (7.5YR/5/4 in the dry state), fresh, compacted, clayey-sandy, granular and crumbly structure, does not carbonate from hydrochloric acid, transition noticeable.

B_{1t} 20- 36 reddish-brown (5YR/3.5/ 6 in dry state), rusty-reddish spots, slightly moistened, dense, medium sandy-clayey, prismatic-lumpy structure, not carbonated by hydrochloric acid, transition noticeable.

B_{2t} 36- 54 reddish-brown (5YR/3/6 in the dry state), rusty-reddish spots, moist, dense, medium sandy-clayey, prismatic-lumpy structure, not carbonated from hydrochloric acid, transition noticeable.

BC 54 - 70 variegated (5YR/4/4 and 5YR/6/4 in the dry state), moist, strongly compacted, medium sandy-clay, lighter than the above, unstructured, does not carbonate from hydrochloric acid.

The humus horizon has a thickness of 18-20 cm.

The soil texture in the surface horizon is clayey-sandy. The amount of physical clay is 17.2%. The soil texture in the illuvial horizon is medium sandy-clayey 39.7 to 42.1%. The amount of silt in the surface horizon is low, while in the illuvial horizon it is several times higher - 32.7 - 36.1%. The predominant fractions are those of silt, medium and fine sand. This soil texture determines poor water permeability, good water retention and unfavorable air regime. According to the amount of organic matter in the surface horizon, the soil is with

low humus content - 0.83%. They have a low reserve of total nitrogen and total phosphorus. Carbonates are not contained in the depth of the entire soil profile. The soil reaction has a strongly acidic pH in H₂O of 5 to 5.3. These soils have a number of unfavorable properties that make them suitable for a limited number of crops - very low humus content, sharp textural differentiation, strongly acidic soil reaction (it can be corrected by liming). They are suitable for growing some less demanding crops.

Eutric Planosols, moderately eroded

They occupy an area of 7688 da, 5.15 % of the total area southeast of the village of Dolna Banya. They are distributed mainly in the central flattened part of the territory of the farm units. They are formed on Pliocene and Tertiary deposits under the influence of forest vegetation. No significant erosion processes are observed in them. Their morphological structure can be observed by the description of a soil profile on a plateau in fruit orchard located 2 km north of Dolna Banya village (Yolevski, M. et al. 1974).

A₁E 0-29 Light gray-brown, fresh, loose, clayey-sandy, small crumble structure, powdery, not carbonated from hydrochloric acid, transition clear.

A₂B(t)g 29-42 light brown, fresh, compact, slightly sandy-clayey, crumble structure, partially dusted by pseudopodzolization, dusted with amorphous silica, not carbonated from hydrochloric acid, simple transition.

B₁(t)cg 42-75 light brown-reddish, moist, slightly dense, slightly sandy-clayey, prismatic, signs of gleying, contains manganese nodules of grains, does not carbonate from hydrochloric acid, transition gradual.

B₂(t)cg 75-115 brownish-reddish, moist, slightly dense, heavy sandy-clayey, prismatic, contains manganese nodules, does not foam from hydrochloric acid, transition noticeable.

C 115-140 light brownish-white, moist, compact, slightly sandy-clayey, unstructured, gravelly, slightly carbonated from hydrochloric acid.

Morphologically, these soils are characterized by weak (20-25 cm) humus horizon with light brown color and dusty from pseudopodzolization and processing small crumbly structure. Dusting with amorphous silica is observed here. Beneath it lies a deep about 70-100 cm alluvial horizon with a reddish dense color, clayey with a prismatic structure and the presence of manganese nodules on water-bearing parts, this horizon is less deep and contains unweathered rocks. Horizon C is almost intact Pliocene Tertiary deposits with light brown to off-white color. The terrain occupied by these soils is flat (with a slight slope) convenient for farm machines.

The soil texture in the surface horizon is clayey-sandy and the amount of physical clay is 18.4%. In the alluvial horizon the soil texture is sharply aggravated - the amount of physical clay is 51.1-62.8%.

The amount of silt in the upper two horizons is low while in the range of the illuvial horizon it is 45.6-57.4%. The predominant fraction of soil profile depth is that of silt followed by the fraction of medium and fine sand. The texture coefficient is 7.8.

This soil texture causes low water permeability, high water holding capacity and unfavorable air regime. The content of humus 0.94% in the surface horizon defines these soils as having low humus. In the lower divisions of the soil profile the amount of organic matter is insignificant - 0.36-0.5%. Carbonates are not contained in the depth of the entire soil

profile. The soil reaction is medium acidic in the surface horizon - pH 5.8 (H₂O). With good farming techniques some less demanding crops can be grown on these soils.

Eutric Fluvisols

They occupy an area of 2919 da - 1.96% of the total area.

They are formed on Alluvial-Deluvial deposits under the influence of meadow vegetation. They have a layered structure characteristic of all alluvial soils. The materials creating the individual layers have a light soil texture. Humus is better expressed in the upper part of the soil profile. The morphological structure of these soils is given by profile 2:

A_I 0-11 light gray-brown (7.5YR/5/6 in the dry state), fresh, loose, slightly sandy-clayey, weakly expressed fine-grained structure, does not carbonate from hydrochloric acid, transition noticeable.

A_{II layer} 11-24 grayish-brown (7.5YR/5/4 in the dry state), slightly moistened, loose, sandy (loose sand), unstructured, does not carbonate from hydrochloric acid, transition noticeable.

A_{III layer} 24-50 grayish-brown lighter than above (7.5YR/5/6 in the dry state), slightly moistened, loose, sandy (loose sand), unstructured, does not carbonate from hydrochloric acid.

The humus horizon has a thickness of 20-30 cm, the amount of organic matter in the humus horizon is 2.17-3.19%. The depth of the soil profile is 60-90 cm. Soil texture in the surface horizon is clay-sandy, the amount of physical clay is 20.1-28.5%. The predominant fractions are coarse particles. This soil texture determines very high water permeability, low water holding capacity and favorable air regime.

The soil reaction is moderately acidic to neutral pH in KCl with value of 5-5.7.

Leptic Cambisols, eroded, stony

Occupy an area of 15688 da - 10.5% of the total area of the study area. They are formed on weathering products on acid rocks under the influence of forest vegetation and active erosion. The profile of these soils is very short and the hard rock is closely laid. They have a light soil texture; they contain a high percentage of skeletal material and a small percentage of organic matter. Due to the very large slope occupied by these soils they are almost economically irrelevant since only individual sections are used.

Our research is based on the analysis of soil samples from the area representing the natural meadow (profile 1), winter cereal - rye (profile 2) with raspberry plantations (profile 2) and left in the prologue, after some years of use (profile 3).

Researched indicators:

Physical and textural parameters:

- soil texture - by pyrophosphate method (by Kaczynski, 1958);
- structure and waterproof aggregates - by sieve analysis dry and wet sieving by the method of NI Savinov (Penkov et al. 1997).

*Agrochemical indicators:

- mobile forms: nitrogen - by the method of Bremner and Kiney; phosphorus - by the method of P. Ivanov; potassium - P. Ivanov (Penkov et al. 1997);
- humus - by the Turin method (Kononova, 1963);
- pH - potentiometrically (in water and in potassium chloride), (Penkov et al. 1997);
- carbonate content - by the Scheibler method (Penkov et al. 1997).

An agrotechnical assessment was performed for the condition of the production areas subject to the study - soil condition in the humus horizon, presence of plant residues, weed density, etc.

Results and Discussion

From the comparative analysis of the results of the laboratory determination of the soil texture, changes in the fractional composition of all studied soil differences are established. For a period of over fifty years, depending on the land use, microrelief and the influence of meteorological conditions, the changes in the main soil horizons are more or less distinctive.

Table 1. Soil texture profile 1 and 54 Dystric Planosols

Horizon and depth (cm)	1.00 - 0.25	0.25 - 0.05	0.05 - 0.01	0.01 - 0.005	0.005 - 0.001	<0.001	Σ <0.01
profile 54							
A ₁ 0-20*	43.2	27.1	11.4	1.9	3.9	11.4	17.2
B _{1t_g} - 20-36*	23.6	24.6	8.4	2.6	3.4	36.1	42.1
B _{2t_g} - 36-54*	23.7	25.6	9.2	2.7	4.3	32.7	39.7
profile 1							
A ₁ -0-20**	39.6	30.8	13.5	2.5	3.1	10.6	16.2
B _{1t_g} -20-36**	29.9	25.7	9.3	2.8	2.9	34.8	40.5
B _{2t_g} -36-54**	29.7	26.3	10.7	2.6	6.1	22.7	31.4

* Note - the data are from the analysis of samples in 1974, Yolevski, M., et al. „Soil characteristics of the land of Dolna Banya – Sofia district, archive of IP ”N. Pushkarov”, Sofia.

** Note - the data are from the analysis of samples in 2019.

A comparative analysis of the data on the soil texture of Dystric Planosols shows that despite the long-term difference between the two studies, the fluctuations in the fractional composition are insignificant (profile 1) .

The long-term impact and sporadic production activity on the land plot did not significantly affect the soil texture of the soil distinction. In the surface horizon, the silt and physical clay content was almost unchanged for the long period between the two analyzes. More significant differences between the fractional composition were found in the B₂ horizon. The content of the silty fraction decreases sharply - by 10%, and the content of physical clay decreases by 8%. Probably in the C horizon there is a porous rock mass in which parts of the fine fractions of the clay have deposited.

Of note is the fact that as a result of the absence of land use the humus content increases - on average by 0.09%. The inclusion of the area in the production activity was for a short time and did not create a risk of surface water erosion.

When comparing the data available from the soil outline and those of made agrochemical analysis indicated that the mobile forms of nitrogen in arable layers is reduced to 4-5 mg / kg soil, and that of useful phosphorus 2.5 times. There is an increase in the useful forms of potassium in the surface horizon, probably due to the decomposition of straw from cultivated cereals. The reaction of the soil solution remains moderately acidic in the surface horizon, but in the B horizon it becomes slightly acidic.

Table 2. Agrochemical properties profile 1 and profile 54 Dystric Planosols.

Horizon and depth (cm)	pH		Carbonates (CaCO ₃)	Base Saturation (V%)	mg / kg	mg / 100 g		Humus %
	H ₂ O	KCL			Total digest. N	P ₂ O ₅	K ₂ O	
profile № 54								
A ₁ 0-20*	5.0	4.1	0,0	65.6	19 , 1	5.6	16.8	0.83
B _{1t_g} 20-36*	5.3	4.3	0,0	66.3	15.5	1.1	18.0	0.77
B _{2t_g} 36-54*	5.1	4.2	0,0	71.4	10.0	0.6	15.9	0.54
profile № 1								
A ₁ 0-20**	5.3	4.3	0,0	62.0	14.2	2.3	22.0	0.88
B _{1t_g} 20-36**	5.5	4.6	0,0	68.4	11.7	0.2	13.3	0.86
B _{2t_g} 36-54**	5.5	4.5	0,0	-	-	-	-	-

* Note - the data are from the analysis of samples in 1974, Yolevski, M., et al. „Soil characteristics of the land of Dolna Banya – Sofia district, archive of IP ”N. Pushkarov”, Sofia.

** Note - the data are from the analysis of samples in 2019.

During the long period between the two studies, profile 2 revealed significant changes in horizons A and B, which are a consequence of the impact of climatic factors and its inclusion in the land fund. Due to the application of a crop rotation system of agriculture through the alternation of cereals oats and rye and trench flax and potatoes, the unification of the soil texture at a depth of up to 42 m is established.

Table 3. Soil texture profile 2 and profile 4 Eutric Planosols.

Horizon depth (cm)	Hygr. moisture %	> 1	1- 0.25	0.25- 0.05	0.05- 0.01	0.01- 0.005	0.005- 0.001	<0.001	Σ <0.01
Profile 4									
AE 0-29*	1.93	0.1	31.6	29.9	18.7	4.1	7	7.3	18.4
A ₂ B _g 29-42*	4.40	1.4	38.3	16.2	13.6	6.9	5.2	15.1	27.2
B _{t_g} 42-75*	-	0	13.2	13.6	7.9	2.5	2.9	57.4	62.8
Profile 2									
AE 0-29 **	3.05	0.0	36.8	37.3	4.9	5.3	6.9	8.8	21
A ₂ B _g 29-42 **	5.36	0.0	37.1	35.6	5.0	5.7	6.5	10.1	22.3
B _{t_g} 42-75 **	-	0.0	5.2	17.4	25.3	10.6	5.3	39.9	55.8
Profile 2									
AE 0-29 ***		0.0	31.4	40.1	5.4	5.9	6.8	10.4	23.1
A ₂ B _g 29-42***		0.0	31.8	37.9	2.1	5.9	8.9	13.4	28.2
B _{t_g} 42-75***		0.0	9.1	15.5	21.8	12.8	7.1	41.4	61.3

* Note - the data are from the analysis of samples in 1974, Yolevski, M., et al. „Soil characteristics of the land of Dolna Banya – Sofia district, archive of IP ”N. Pushkarov”, Sofia.

** Note - the data are from the analysis of samples in 2019 from levels with three crop rotation

*** Note - the data are from the analysis of samples 2019 perennial plantation - raspberries

Unlike the initial data, where the process of pseudopodzolization is visibly outlined in the three horizons, in the analysis in 2019 there is a visible textural boundary between A and B horizon, as the content of silt is 4.5 times higher and physical clay over 3 times. In land use with perennial plantations - raspberries, a higher content of silt and physical clay is found in

the A₂B horizon, as compared to the levels with predominant cultivation of cereals and cereal-legume mixtures, the physical clay has a 5% increase. A probable reason is the fact that during the creation of the raspberry plantation deep plowing was performed, followed by plowing in the rows every year while during the three-field crop rotation the depth of cultivation is up to 20 cm.

The chemical properties data for the two surface horizons outline some trends. The reaction of the soil solution of weakly acidic to neutral after long period becomes moderately acid (5.5-6.2 in H₂O). This change is due to natural acidification processes under the influence of water from the adjacent forest vegetation and not from production activity. The land section has been artificial meadow, which then becomes a natural grass. The soil is depleting of bases in the surface horizon, despite the percentage increases in the depth, reaching 78.0%.

Table 4. Chemical properties Profile № 2 and Profile № 4 Eutric Planosols

Horizon and depth (cm)	pH		Carbonates (CaCO ₃)	Base Saturation (V%)	mg/ kg	mg/100 g		Humus %
	H ₂ O	KCL			Total N	P ₂ O ₅	K ₂ O	
Profile 4								
AE 0-29*	5.8	5.0	0.0	65.6	18.0	8.3	22.6	0.94
A ₂ Bg 29 – 42*	6.7	5.7	0.0	70.4	16.2	5.4	19.7	0.5
Btg 42 -75*	6.5	5.6	0.0	77.0	9.6	1.2	14.8	0.43
Profile 2								
AE 0-29 **	5.5	4.7	0.0	55.7	16.6	1.8	19.0	1.05
A ₂ Bg 29 – 42**	6.2	5.2	0.0	78.0	12.0	0.2	15.6	0.68
Btg 42 -75**	-	-	0.0	-	-	-	-	-
Profile 2								
AE 0-29 ***	5.8	4.9	0.0	62.8	25.3	3.0	20.1	1.01
A ₂ B 29 – 42***	6.3	5.5	0.0	65.0	20.5	0.6	16.8	0.68
Btg 42 -75***	-	-	0.0	-	-	-	-	-

* Note - the data are from the analysis of samples in 1974, Yolevski, M., et al. „Soil characteristics of the land of Dolna Banya – Sofia district, archive of IP ”N. Pushkarov”, Sofia.

** The data are from the analysis of soil sample from 2019 from a field with three crops rotation

*** The data are from the analysis of soil sample from 2019 with permanent crop raspberries

During the long-term land use of the area it is established that during the raspberry plantation the assimilable forms of nitrogen increase, as for the horizons to a depth of 42 cm it is respectively 5.8 mg/kg of soil. In the absence of balanced fertilization, the mobile forms of phosphorus and potassium decrease and it is more significant for the amount of P₂O₅- 4.5 times in the area with three crop rotation and about 3 times in the area occupied by raspberries. We assume that when creating the perennial plantation, basic fertilization with phosphorus and potassium was performed.

Pseudopodzolic soils differences, in addition to a pronounced textural differentiation, are also characterized by a weak humus horizon and an acid reaction of the soil solution (Koynov et al., 1972). The treatment of these soils should be carried out during time of appropriate humidity to avoid some adverse physical and mechanical consequences. The arable land can be deepened to 25-30 cm with the application of manure and higher doses of

mineral fertilizers. When using mineral fertilization priority should be given to fertilizers with physiologically alkaline actions.

The structure of the Fluvisols (Alluvial-Deluvial) soil is layered, with stratum which is formed under the influence of the flowing waters of the Maritsa River. Subsequently, the river withdrew to its current bed, and a process of deluvial formation began on the terrain. Of note is the fact that the percentage of coarse sand is increasing - by 15.7% and 21.8% respectively for A_I layer. and A_{II} layer. horizons.

Table 5. Soil texture profile № 3 and profile № 46 Eutric Fluvisols

Horizon depth (cm)	Hygr. moist ure %	Amount > 1	1-0.25	0.25-0.05	0.05-0.01	0.01-0.005	0.005-0.001	<0.001	Σ <0.01
profile № 46									
A _I 0-11*	2.53	13.3	31.5	21.2	11.7	4.5	5.6	10	20.1
A _{II} 11-24*	5.20	42.7	33.1	18.2	0.5	1.5	1.9	11.9	15.3
A _{III} 24-50*	-	79.2	15.4	4.2	0.3	0.2	0.2	6.2	16.6
profile № 3									
A _I 0-11**	2.18	0.0	35.0	36.9	4.5	5.5	6.4	11.7	23.6
A _{II} 11-24**	2.60	0.0	32.2	40.0	3.7	5.5	6.4	12.2	24.1
A _{III} 24-50**	-	0.0	15.0	14.4	9.3	6.6	3.3	19.9	29.8

* Note - the data are from the analysis of samples in 1974, Yolevski, M., et al. „Soil characteristics of the land of Dolna Banya – Sofia district, archive of IP ”N. Pushkarov”, Sofia.

** Note - the data are from the analysis of soil samples in 2019.

Based on microrelief, it can be assumed that this change in the soil texture is due to the surface water erosion with the adjacent land plot of asphalt road the soil was moved to declines forming the ravine of the river. A profile made in an adjacent pine grove gives grounds for such an assumption.

Table 6. Chemical properties profile 3 and profile 46 Eutric Fluvisols

Horizon and depth in cm	pH		Carbonates (CaCO ₃)	Base Saturation (V%)	Humus %
	H ₂ O	KCL			
profile 46					
A _I 0-11*	6.4	5.7	0.0	78.0	2.17
A _{II} 11-24*	6.7	6.0	0.0	76.6	1.45
A _{III} 24-50*	6.8	6.0	0.0	-	-
profile 3					
A _I 0-11**	6.1	5.2	0.0	67.3	1.78
A _{II} 11-24**	6.3	5.5	0.0	72.4	1.39
A _{III} 24-50**	6.7	-	0.0	-	-

* Note - the data are from the analysis of samples in 1974, Yolevski, M., et al. „Soil characteristics of the land of Dolna Banya – Sofia district, archive of IP ”N. Pushkarov”, Sofia.

** Note - the data are from the analysis of soil samples in 2019.

The chemical properties are characterized with slightly acidic to neutral pH in soil research in cooperative farm Dolna Banya which in 2019 showed a decrease to medium

acidic soil solution. Carbonates are washed deep into the profile and base saturation slightly decreased as a result of the impact of climatic factors. In the event of the water erosion the humus content is reduced of the Eutric Fluvisols, as for long-term decrease was respectively 0.39% and 0,06% for the first and second layer of the soil profile.

Conclusion

For a long period of time there were changes in the surface soil horizons of all studied differences of soils. The process of pseudopodzolization continues to develop in Planosols. It is observed an increase in the content of silt in the horizons located below the humus horizon. In the case of Eutric Fluvisols (Alluvial-Deluvial), an increase in the fraction of coarse and fine sand and a decrease in the humus content are reported. Land use has an impact on the soil texture in the case of moderately eroded Dystric Planosols. In the deeper horizons, when planted with raspberries, the content of silt and physical clay increases compared to the same soil difference in the area with the application of three crop rotation, compacted with cereals with a subsided surface. The content of mobile forms of nitrogen increases in the area with permanent planting. The useful for plants forms of phosphorus and potassium decrease more significantly in the area on which three crop rotation cultivated with cereals with a mouldboard ploughing for growing is applied.

References

- Blum, W. (2005). Indicators of sustainable use of soil resources. *Proceedings of the National conference with international participation "Management, use and protection of soil resources*, Sofia, 15-22.
- Boneva, K., Houbenov, G. (2005). Mineralogical composition of the ordinary, Al.-Fe humus and hydromorphous mountain - meadow soils of Rila mountain. *Proceedings of the National conference with international participation "Management, use and protection of soil resources*, Sofia, 202-206. (in Bulgarian)
- IUSS Working Group WRB. (2015). World Reference Base for Soil Resources 2014, update 2015 International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.
- Kachinskiy, N.A. (1958). *Mechanical and Microaggregate Texture of Soil, Methods of its Study*. Pub. A.S. USSR, S. 25, Moscow, 191. (in Russian)
- Kinoshita, R., Schindelbeck, R. & van Es, H. (2017). Quantitative soil profile - scale assessment of the sustainability of long-term maize residue and tillage management. *Soil and Tillage Research*, 174, 34-44.
- Koynov, V., Trashliev, H., Yolevski, M., Ninov, N., Gyurov, G. (1972). Bulgaria's soil resources and their use. *First National Congress of Soil Science*, ed. of BAS, Sofia, 476. (in Bulgarian).
- Kononova, M. (1963). *Soil organic matter. It's nature, properties and methods of study*. ANSSSR, Moskva 314p. (in Russian)
- Krastanov, S. (2006). International system for assessment of sustainable land management. (translate from A. Smyth and J. Dumanski). *Minerva Publishing House*, Sofia, 107. (in Bulgarian).

Ninov, N. (2007). On characteristics and criteria for investigation, diagnostics and mapping of soils cover in karst regions of Bulgaria for the GIS purposes. *Proceedings of the International Conference "60- years Institute of Soil Science" N. Poushkarov "*, 73-74. (in Bulgarian)

Ninov, N., Andonov, T., Kolchakov, I., Teoharov, M. (1985). Classification, diagnostics and problems of mountain soils in Bulgaria. *International Conference on the Classification and Use of Soils from Mountain Areas*, 40-52. (in Bulgarian)

Penkov, M., Daskalova, A., Mondeshka, M. (1997). *Guidelines of soil science*, UABG, Sofia, 203p. (in Bulgarian)

Penkov, M., Banov, M., Yurdanov, C., Teoharov, M. (2001). Perspectives and priority tasks of soil science. *Soil science, agrochemistry and ecology*, 4-6, 13-15. (in Bulgarian).

Teoharov, M. (2004). Corelation of soils indicated in map and classification of Bulgaria with World Reference Base (WRBSR, 2002). *Soil science, agrochemistry and ecology*, 4, 3-13. (in Bulgarian).

Teoharov, M. et al., (2019). *Genetic and applied classifications of soils and land in Bulgaria*, Bulgarian soil science society, Sofia, 212. (in Bulgarian).

Ugarte, C., Nicolardot, B., Quinche, M., Munier, N. & Ubertosi, M. (2016). Effects of integrated management based cropping systems on the water retention of a silty clay loam soil. *Soil and Tillage Research*, 156, 74-82.

Yolevski, M., et al. (1974). „Soil characteristics of the land of Dolna Banya – Sofia district, archive of IP ”N. Pushkarov”, Sofia. (in Bulgarian)



Influence of Environmental Variables on Carbon Mineralization in Diverse Soil Management Systems Under Maize Cropping in Kwara State, Nigeria

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Abstract

Understanding the influence of agricultural soil management practices on soil processes and the environment is vital for sustainable food production. Therefore, this study evaluated the impact of soil temperature and moisture on soil organic carbon mineralisation under synthetic (NPK) and organic (biochar) amendments in a maize cropping system in Ilorin, Southern Guinea Savanna of Nigeria. The objectives were to determine the C mineralisation and C sequestering potential under each amendment and assess how precipitation amounts and soil temperature influence carbon mineralisation. Two soil types (Anthrodensic Ustorthent and Typic Ustorthent) were used, and four treatments (control, NPK, biochar+NPK, and biochar) replicated thrice were laid out in completely randomised design on each soil. Soil respiration was measured in-situ by the alkali absorption method. Data collected was subjected to analysis of variance procedure for complete randomized design to determine significant differences in treatment means, correlation and regression analyses were also carried out to test the relationships amongst experimental factors and variable responses. Results showed that evaluated nutrient management options did not significantly influence C mineralisation. C mineralisation, however, differed between soils, with Typic Ustorthent having higher organic carbon (OC), total CO₂ emission (82.35 mg) and mean CO₂ emission rates (1.18 mg m⁻² d⁻¹). Correlation analysis showed differing relationships between soil temperature and C mineralisation under the different treatments and soils, with significant positive correlation ($r=0.44$; $p \leq 0.05$) recorded only under sole biochar treatment in the Typic Ustorthent. Rainfall amounts had no significant correlation with C mineralisation.

Keywords: C mineralisation, C sequestration, Entisols, rainfall, temperature, SOC

Introduction

Soil organic carbon (SOC) plays an essential role in the stability and fertility of soils (Trivedi *et al.*, 2018) and exists in inorganic and organic forms. Soil C plays a crucial role in the terrestrial carbon cycle, releases nutrients for plant growth, promotes soil structure, biological and physical health, and is a buffer against harmful substances. These make maintaining optimum amounts of OC in soil paramount for sustainable agricultural production.

Land management options present opportunities for good agricultural soil resource use, sustainable food production and sustenance of livelihoods. In this regard, optimum soil management under crop production is desirable for good yield and minimised adverse environmental effects. Previous studies have shown that land management is closely linked to SOC turnover (Jamala and Oke, 2013; Xiao *et al.*, 2017), which has a far-reaching impact on terrestrial carbon cycles and connected ecological implications such as climate change.

In an earlier study, Vanden *et al.* (2003) showed that SOC content is lost principally in the form of CO₂, following the conversion of natural land states for agricultural use. However, carbon-enhancing land management helps improve the carbon sink potential of soils (Ding *et al.*, 2014). , the C sink or source potential of soil thus depends on soil physical and chemical factors influenced by land management, which impact soil functions and affect the activities of soil microbial populations that decompose SOM and make the nutrients available to plants (Guo *et al.*, 2017).

Climatic variables are another critical set of factors determining C turnover in soil. Research has shown that soil temperature and moisture affect microbial activity, surface runoff, land surface energy dynamics, root zone productivity, and biomass yield (Hacki *et al.*, 2005), all of which bear C turnover in soil. Soil water also enhance dissolved organic carbon (DOC) leaching from the forest floor, a vital C pool. Temperature and precipitation are dominant factors affecting soil organic carbon storage (Herold *et al.*, 2014).

Understanding the interaction between climatic factors and management options is thus important to design tailored land management approaches that guarantee increased food production and SOC buildup. This is especially important under maize production due to its centrality as one of the world's most important food/ feed and industrial use crops. Therefore, this study is designed to assess the effect of variable nitrogen, phosphorus and potassium compound fertilisers application rates and biochar amendment under conventional tillage practices for their C sequestration potential.

Low nutrient content and accelerated mineralisation of SOM remain two significant constraints facing sustainable agriculture, as earlier identified by Renner (2007). In the face of high human population growth, especially in sub-Saharan Africa, intensified agricultural management has become inevitable. This reality makes studies aimed at optimising land management under prevailing climatic conditions pertinent. We hypothesise that biochar addition will lower SOC mineralisation, and N fertilisation will increase C mineralisation in the test soils.

Materials and Methods

Description of the study area

This study was carried out within the University of Ilorin Teaching and Research Farm in Ilorin, Kwara State, in Southern Guinea Savannah (SGS) agroecological zone of

Nigeria (Figure 1). Geographically, the state is located between latitudes $7^{\circ} 45'$ and $9^{\circ} 30'$ North of the Equator and Longitudes $2^{\circ} 30'$ and $6^{\circ} 25'$ East of the Prime meridian. The SGS zone has a mean annual rainfall of 100–150 cm and a wet season lasting 6–8 months between March and October (Table 1).

The climate is tropical and is characterised by double rainfall maxima tropical wet and dry weather. Temperature is uniformly high and ranges between 25°C and 30°C in the wet season, and dry season temperature ranges between 33°C and 34°C . Relative humidity in the wet season is between 75 to 80 %, while about 65 % in the dry season.

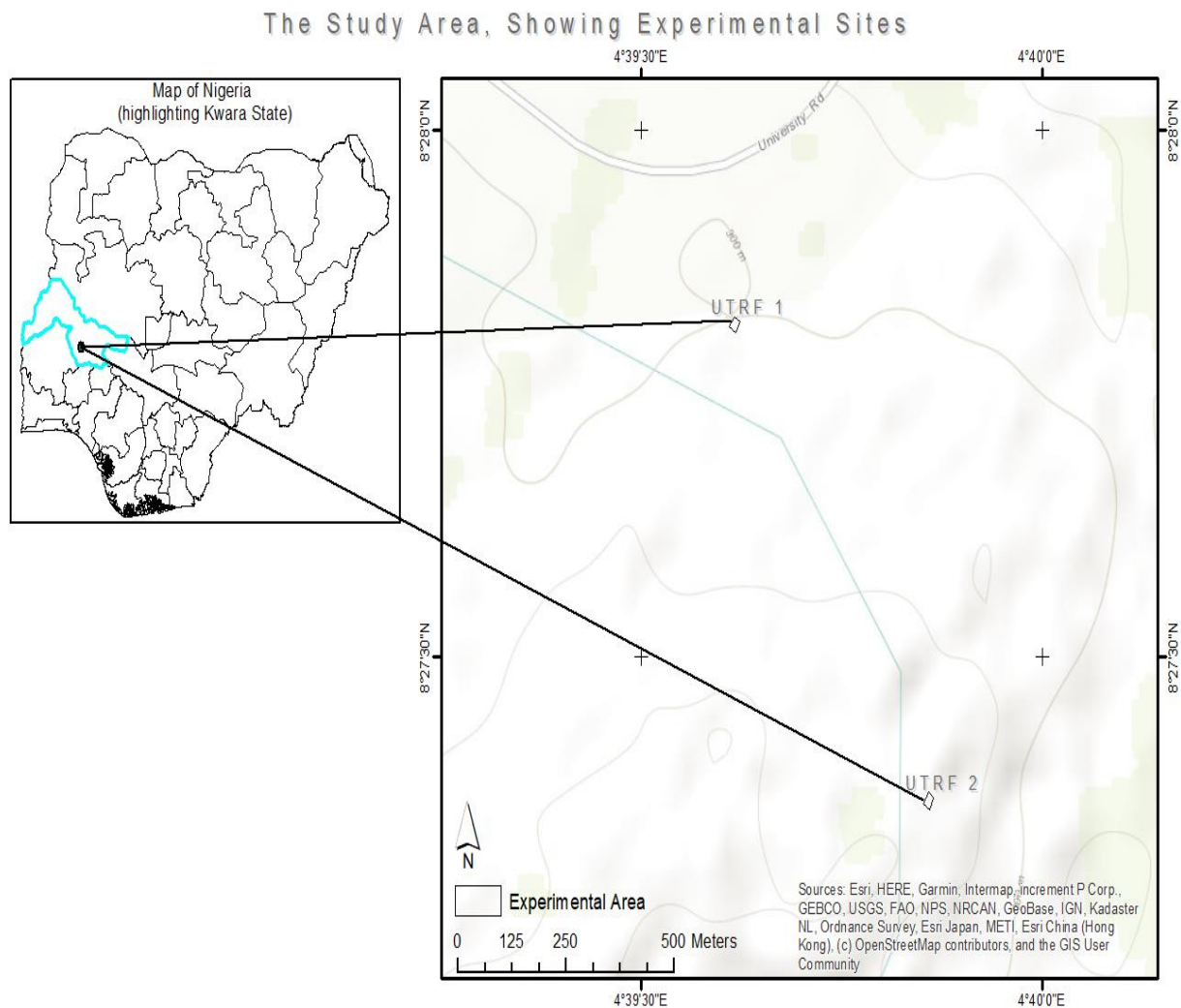


Fig. 1: Map showing the study area and experimental locations

The state is considered one of the essential rainfed agricultural areas in semi-arid regions of the country and could be defined as dependent mainly on rainfall for crop production. Food crops produced are mostly maize, rice, sorghum, yam, cassava, water yam and sweet potato, which constitute the main staple foods (Ajadi *et al.*, 2011). To a lower extent, the soils are formed majorly from basement complex rocks (metamorphic and igneous rocks) and sedimentary rocks. The metamorphic rocks include biotite gneiss, banded gneiss, quartzite augite gneiss and granitic gneiss. The intrusive rock includes pegmatite and vein quartz (Olaniyan and Ogunkunle, 2007).

Table 1. 1989 – 2014 monthly rainfall data for Ilorin (Source: Ilorin airport meteorological station)

Years	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Total
1989	0.0	0.0	56.2	96.5	106.8	239.9	111.3	199.9	233.8	188.9	0.0	0.0	1233.4
1990	0.0	8.5	0.0	158.2	130.7	129.7	150.0	116.8	225.1	98.7	17.4	0.0	1035.1
1991	17.2	17.6	37.8	67.5	340.8	135.9	9.0	138.8	124.8	127.0	0.0	0.0	1326.7
1992	0.0	0.0	2.0	46.7	166.6	90.1	134.7	75.9	129.4	193.2	0.0	0.0	838.6
1993	0.0	102.5	79.0	35.2	176.1	220.6	100.4	333.6	362.8	84.9	0.0	0.0	1495.0
1994	70.1	0.0	7.9	161.0	168.0	168.1	283.1	83.4	201.0	317.9	289.9	0.0	1750.4
1995	0.0	0.0	79.0	79.0	234.0	186.5	140.5	245.1	272.5	133.0	11.5	12.0	1393.1
1996	0.0	0.0	56.5	67.1	165.3	154.2	96.4	154.6	199.8	96.3	0.0	0.0	990.2
1997	0.0	0.0	93.1	206.4	207.4	375.2	158.8	107.6	224.4	115.3	15.0	0.0	1503.2
1998	0.0	0.8	17.1	73.9	159.6	132.3	58.5	170.9	224.8	140.0	0.0	0.0	977.9
1999	0.0	32.5	54.9	67.1	143.3	244.9	195.6	85.7	265.6	182.5	22.8	0.0	1294.9
2000	0.0	2.2	2.4	22.8	68.2	262.2	93.4	163.9	268.0	9.0	0.0	0.0	892.1
2001	0.0	0.0	18.0	45.0	139.0	121.8	138.7	44.5	176.4	60.8	0.0	0.0	744.2
2002	0.0	0.0	59.4	163.2	57.2	97.8	180.8	182.7	144.5	176.7	6.5	0.0	1068.8
2003	0.0	14.0	12.4	93.9	124.5	360.7	123.2	130.9	176.2	133.4	46.7	0.0	1215.9
2004	18.2	33.1	4.0	67.0	260.5	159.2	211.4	145.4	243.5	98.1	31.6	0.0	1272.0
2005	0.0	5.5	25.5	75.7	187.6	171.0	130.2	93.6	282.6	109.8	10.5	0.0	1092.0
2006	1.2	16.1	27.5	106.6	163.7	259.6	224.1	88.2	276.2	190.0	0.0	0.0	1353.2
2007	0.0	7.0	22.0	115.0	306.2	227.7	205.3	189.9	236.2	162.5	0.0	2.5	1474.3
2008	0.0	0.0	9.5	123.5	35.2	184.1	394.1	329.5	343.6	88.6	3.4	5.2	1516.7
2009	6.0	0.5	19.6	219.2	112.1	170.6	249.5	226.0	231.0	112.0	47.4	0.0	1393.9
2010	0.0	6.5	60.9	58.2	112.2	45.1	139.1	123.7	228.3	226.4	2.0	0.0	1002.4
2011	0.0	19.1	4.8	13.5	169.1	231.8	220.2	294.5	334.6	163.2	0.0	0.0	1450.8
2012	26.0	0.0	0.6	173.3	205.7	162.8	202.6	168.1	200.8	84.4	0.0	7.2	1231.5
2013	0.5	39.0	39.8	181.8	81.8	132.9	107.3	17.7	202.5	154.3	0.0	11.4	969.0
2014	6.3	34.2	71.0	321.4	163.8	154.7	82.1	94.9	391.6	259.4	0.0	0.0	1579.4
MEAN	5.6	13.0	33.1	109.2	161.0	185.4	159.2	154.1	238.5	142.6	19.4	1.5	1234.4

Soil Survey

A free soil survey identified two soil types within the study area. Profile pits were dug and described, following United States Department of Agriculture (USDA), Soil Survey Staff guidelines (2017). Soil classification was done following USDA Soil Survey Staff (2014) guidelines. Identified soils were labelled UTRF 1 and UTRF 2 at approximately 8°27'48.91"N 4°39'37.01"E and 8°27'21.76"N 4°39'51.53"E respectively. The soils were classified as Anthrodensic Ustorthent and Typic Ustorthent, respectively, based on observed morphological and measured physical and chemical properties.

Laboratory Analysis

Top (0 – 130 cm) and profile horizons soil samples were air-dried, 2 mm sieved, and subjected to physical and chemical analyses following procedures outlined in Table 2. The biochar was made out of hardwood in a top-lit updraft kiln at ~350 °C. Biochar samples were broken, ground (using a ceramic mortar and pestle) and passed through a 0.5 mm sieve mesh before analyses. Analyses procedures are presented in Table 2. The soils' morphological, physical and chemical properties are shown in Tables 3 and 4, respectively, and biochar properties in Table 5.

Table 2. *Methods of soil and biochar samples analyses*

Parameter	Method of Analyses	
	Soil	Biochar
Soil particle size fractions	Gee and Or, 2002	
pH	Thomas (1996)	In 0.1 N KCl solution (1:10 wt/wt) ratio
Total Nitrogen	Bremner, 1996	Enders and Lehmann (2012)
Organic carbon	Walkley and Black, 1934	Enders and Lehmann (2012)
Available phosphorus (Bray 1-P):	Bray and Kurtz (1945)	Enders and Lehmann (2012)
Exchangeable bases (Ca, Mg, K, and Na)	1 N ammonium acetate (NH ₄ OAc) extraction	Enders and Lehmann (2012)
ECEC	Juo et al. (1976)	
Exchangeable acidity	Peech et al., 1962	
Percentage base saturation	Summation of total exchangeable bases expressed as a percentage of CEC	
Moisture content		ASTM E871-82
Volatile matter		ASTM E871-82
Ash		ASTM E871-82
Fixed carbon		ASTM E871-82

Table 3. Morphological properties of soil profile pit horizons

Pedon	Horizon designation	Depth (cm)	Colour (moist)	Texture +	Structure ++	Mottles +++	Drainage ***	Boundary **	Consistence *	Artifacts ^	Roots ^v	Landform/topography
UTRF1	Ap	0-20	10 YR 2/2 (very dark brown)	I	Mo, vs, sab	N	III	d, s	m, lo; w, nst, npl	A	C co	Undulating
	B ₁	20-40	10 YR 5/4 (yellowish brown)	fs	Mo, me, sab	N	III	d, s	m, lo; w, ssp	A	C, md	
	B ₂	40-60	10 YR 4/4 (dark yellowish brown)	g, cl	Mo, me, ab	N	III	d, s	m, fr; w, ssp	A	F, co	
	Bv	60-115	2.5 YR 4/8 (red)	g, cl	Mo, me, ab	N	III	d, s	m, lo; w, ssp	A	F, vfi	
UTRF2	Ap	0-10	10 YR 4/3 (brown)	I	Mo, vf, sab	N	III	d, b	m, lo; w, ssp	A	F, vfi	Undulating
	B ₁	10-40	10 YR 4/4 (dark yellowish brown)	g, cl	Mo, c, sab	N	III	d, b	m, fr; w, ssp	A	C, vfi	
	B ₂	40-90	7.5 YR 4/6 (strong brown)	g, cl	wm, me, sab	N	III	d, b	m, lo, w, ssp	A	Vf, vfi	
	Bv	90-133	2.5 YR 5/6 (red)	g, cl	Mo, me, ab	A, co, cl	II	d, s	m, lo; w, spl	A	F, vfi	

DESCRIPTION KEYS

Texture +: b= boulder; s= stony; g= gravelly; cs= coarse sandy; fs= fine sandy; sl= silty; cl= clayey; l= loamy. Structure ++: we=weak; mo=moderate; st=strong; wm=weak to moderate; ms= medium to strong; c= coarse; f= fine; g= granular; cr= crumbs; sg= single grained; pl= platy; sab= sub-angular blocky; ab= angular blocky. vs= very small, me=medium. Mottles +++: n=none; v= very few; f=few; c=common; m=many; a=abundant; vf= very fine; md= medium; co=coarse; fa=faint; d=distinct; p=prominent; s= sharp; cl=clear; d=diffuse. Consistence *: m= moist; w=wet; fr= friable; fi=firm; st= strong; l=loose; c=crumbly; sst= slightly sticky; sp=slightly plastic; s=slick; p=plastic; nst= non-sticky; npl= non plastic, lo=loose, ssp=sticky and slightly plastic. Boundary **: c= clear; s= smooth; g= gradual; d= diffuse; w= wavy; di= breakage (Discontinuous). Drainage ***: I= swamp; II= poorly drained; III=well drained. Artifacts ^: P= Present; A= Absent. Roots ^^: V= Very few; F= Few; C= Common, M= Many. vfi= Very fine; fi= Fine; md= Medium; co= Coarse, A = Absent

Table 4. Physical and chemical properties of soil profile pit horizons

Soil	Hor	Depth	Silt (%)	Clay (%)	Sand (%)	pH (H ₂ O)	pH (KCl)	EC (μS cm ⁻¹)	Av. P (%)	C (%)	N (%)	EA	Ca	Na	Mg (cmol(+) Kg ⁻¹)	K	ECEC	BS (%)
UTRF 1	A	0-20	2.0	8.48	89.52	7.18	6.52	42.00	6.74	2.82	0.08	0.96	1.97	3.69	1.48	0.55	8.64	88.93
	B ₁	20-40	2.0	8.48	89.52	7.44	6.28	80.00	6.82	2.78	0.01	0.48	4.75	3.37	2.15	0.89	11.64	95.88
	B ₂	40-60	12.0	8.48	79.52	6.56	6.13	58.00	7.23	2.60	0.02	0.53	1.19	1.85	2.50	0.91	6.91	92.42
	Bv	60-115	6.0	12.48	81.52	7.80	6.12	132.00	7.01	3.18	0.05	0.50	1.97	2.92	1.63	0.69	7.71	93.56
UTRF 2	A	0-10	2.0	8.48	89.52	6.82	6.50	5.08	6.72	3.04	0.07	0.82	0.41	2.91	1.74	0.91	6.79	87.93
	B ₁	10-40	12.0	10.48	77.52	6.80	6.77	18.00	7.28	2.89	0.07	0.06	1.56	3.19	1.92	1.06	8.33	92.80
	B ₂	40-90	10.0	18.48	71.52	7.19	5.82	38.00	7.32	2.58	0.08	0.32	2.03	1.93	2.17	1.08	7.54	95.70
	Bv	90-115	2.0	8.48	89.52	7.57	6.33	52.00	6.82	2.05	0.07	0.46	1.94	2.80	2.89	0.97	9.05	94.92

EA: exchangeable acidity; BS: base saturation

Table 5. *Properties of biochar material*

pH (H ₂ O)	10.22
pH (KCl)	9.24
Electrical Conductivity (µS/cm)	5.08
Available Phosphorus (mg/kg)	5.59
Organic Carbon (%)	34.08
Nitrogen (%)	0.28
Ca (cmol/kg)	1.99
Na (cmol/kg)	0.30
Mg (cmol/kg)	1.55
K (cmol/kg)	2.10
ECEC (cmol/kg)	6.60
Ash content (%)	24.3
Moisture content (%)	4.21
Fixed carbon (%)	48.96
Volatile matter (%)	22.53

Field Experiment

The field experiment was conducted in the rainy season of 2019 (August – Nov.). It was laid out in a Complete Randomized Design (CRD) on each soil. Four treatments were used; control (C), NPK 20:10:10 at 600 kg/ha (NPK), biochar at 3.5 t/ha + NPK 20:10:10 at 600 kg/ha (biochar+NPK), and biochar at 3.5 t/ha (B). Treatments were replicated thrice on plots measuring 2 x 4 m (8 m²) and separated by a buffer of 1 m between plots. In NPK plots, 200 g was applied and 400 g at 6 weeks after planting. Biochar was applied after tillage, before planting, and control treatments were not treated with any amendment. Quality protein maize (QPM), a hybrid variety, was planted immediately after amendments. Seeds were sown at 2 seeds per hole, 25 cm within the row and 75 cm between row spacing. Hand weeding was done at 21 days, 6 and 9 weeks after planting (WAP). The second NPK split application was made at 6 (WAP)

Carbon Mineralisation Measurement

Soil respiration was measured in situ using the alkali absorption method, using the non-flow-through steady-state (static chamber) system (Hopkins, 2006). Field chambers were constructed using a PVC non-reactive material following the USDA Agricultural Research Service guidelines in Parkin and Venterea (2010). Permanent chambers (10.6 cm diameter Polyvinyl Chloride (PVC) pipes of 30 cm height were installed to 20 cm depth) in the centre of each treatment plot at spots cleared of all organic matter residue. Three chambers were

used as blanks. Carbon dioxide emission was trapped in 60 mL plastic vials containing 40 mL 0.25 M NaOH. Five millilitres (5 mL) aliquots of the trapping solution (0.25 M NaOH) were back-titrated to a colourless end-point with 0.15 M HCl after precipitation of carbonates by adding 8 mL 3M BaCl₂ using phenolphthalein as an indicator (Haber, 1958). CO₂ was sampled on days 1, 3, 6 and every three days intervals till the maturity of the test crop.

CO₂-C was evaluated using the equation:

$$CO_2 - C = ((B - V) \times M \times E) / (A \times T)$$

Where:

CO₂-C = C efflux (mg m⁻² d⁻¹); B = volume of HCl solution used for the titration of treatment samples (mL); V = volume of HCl solution used for the titration of blank samples (mL);

M = molarity (mol L⁻¹) of the HCl solution; E = carbon gram-equivalent (6 g);

A = exposed soil surface area (m²); and T = sampling time (d).

Meteorological Data

Rainfall (total rainfall between gas sampling times) and soil temperature (mean 0-20 cm) data was obtained from the University of Ilorin Teaching and Research Farm Meteorological station. The meteorological station is 1.6 and 0.4 km away from UTRF 1 and 2 respectively.

Data Analysis

Data collected on C mineralisation was subjected to analysis of variance (ANOVA) at $p = 0.05$. In contrast, rainfall, soil temperature and carbon mineralisation data were subjected to Pearson Correlation (r) analysis to explore the relationships between the variables. Calculations were done in SPSS 20th Edition.

Results and Discussion

Variation in C Mineralization and CO₂ Emission Treatments and Soils

Table 6 shows the results of the analyses of variance of means of experimental factors. The highest CO₂ emissions were recorded under NPK treatment (79.856 mg), while the least was in the biochar alone treatment at 74.845 mg. However, the differences in the values for all treatments were not significant at $p \leq 0.05$. CO₂ emission rate followed a similar trend with that of total emissions, having no significant difference among treatment applications. Soils, however, exerted significant variations both in total CO₂ emission and emission rate. The highest values were recorded in UTRF 2, with observations of 82.351 mg and 1.183 mg m⁻² d⁻¹ for total CO₂ emission and mean emission rates, respectively. These values were significantly higher than those recorded in UTRF 1 at $p \leq 0.01$ and $p \leq 0.05$, respectively. No significant interactions were recorded between experimental factors.

The observations recorded showed that sole NPK treatment and that incorporated with biochar resulted in higher C mineralisation. This observation is different from the findings of Olaniyan et al. (2020) in their evaluation of biochar C stability in soils around the same geographical location as in this study. In their research, they found that SOC and biochar C mineralisation was lower in soils of higher organic N, and they attributed their finding to the possible toxicity effect of high N on soil C degradation microbial communities. However, the N contents of the soils in the study are much higher than those in this research. This may explain the variation observed. At lower soil N levels, N addition may increase microbial population and activities rather than inhibit it, which will result in higher N mineralisation.

The finding also differs from that of Perveen et al. (2019) but is consistent with that of Wang et al. (2015), which reported that N enrichment resulted in higher CO₂ release in croplands. The variation in C mineralisation responses between soils can be attributed to differences in properties. While both soils are comparable in properties, especially soil physical (particle size fractions) with a similar range in sand silt and clay components, UTRF 1 had a higher OC amount. This can be attributed to the propensity of low OC soils to better adsorb soil C on soil clay mineral surfaces, which makes it less free for microbial degradation. Kimetu et al. (2009) also reported that amended C is less accessible for microbial utilisation in low N and C soils.

Table 6. Variation in means of CO₂ emissions in treatments and soils

	Total CO ₂ emission (mg)	Mean CO ₂ emission rate (mg m ⁻² d ⁻¹)
Treatment		
B	74.845	1.072
Biochar+NPK (BN)	78.964	1.134
C	77.494	1.125
NPK	79.856	1.157
<i>F-value</i>	0.512	0.696
<i>p-value</i>	0.680 NS	0.568 NS
Soil		
UTRF 1	73.228	1.061
UTRF 2	82.351	1.183
<i>F-value</i>	8.870	7.828
<i>p-value</i>	0.009 **	0.013 *
Interaction		
T x S	0.510 NS	0.382 NS

*: significant at $p \leq 0.05$, **: significant at $p \leq 0.01$, NS: not significant

Relationship Between Soil Temperature and C Mineralization in Soils and Treatments

Fig. 2 shows topsoil (0 – 20 cm) temperature and CO₂ emission rate trends in treatments and soils. There was no clear trend in C mineralisation and emissions in both soils with soil temperature. The general direction was highly fluctuating emission rates at the start of incubation before a stabilisation at about day 45 and 57 in UTRF 1 and 2, respectively. This observation largely conforms with previous findings of a more variable emission at the start of incubation and a steady progression with time (El-Naggar et al., 2015; Olaniyan et al., 2020).

However, correlation analyses showed that the relationship between soil temperature and C mineralisation differed between treatments and soils. In Table 7, which presents the results of correlation analysis on an individual soil basis, there was a significant positive relationship between soil temperature and SOC mineralisation under biochar (B) treatment ($r=0.44$; $p=0.03$; $N=24$) in UTRF 2, whereas the relationship was not significant in UTRF 1,

and the correlation was negative. No other correlation for the different treatments was substantial.

A general correlation analysis (Table 8) irrespective of soils also showed that soil temperature had a significant positive correlation with C mineralisation rate under biochar treatment ($r=0.29$; $p=0.04$; $N=24$), and the same observation as in the soil-wise analysis was observed, with no significant correlation under other treatments. Although insignificant, the relationship between soil temperature and C mineralisation was positive under all experimental treatments. This finding aligns with that of Benbi and Khosa (2014), in who they found that incubation medium temperature significantly influenced C mineralisation. Although they also noted that the chemical composition of the C source also determines how much effect temperature has on C mineralisation. This also applies in the current study. The variation in inherent C sources in the soils can be attributed to the difference in the relationships observed between soil temperature and C mineralisation in the two soils.

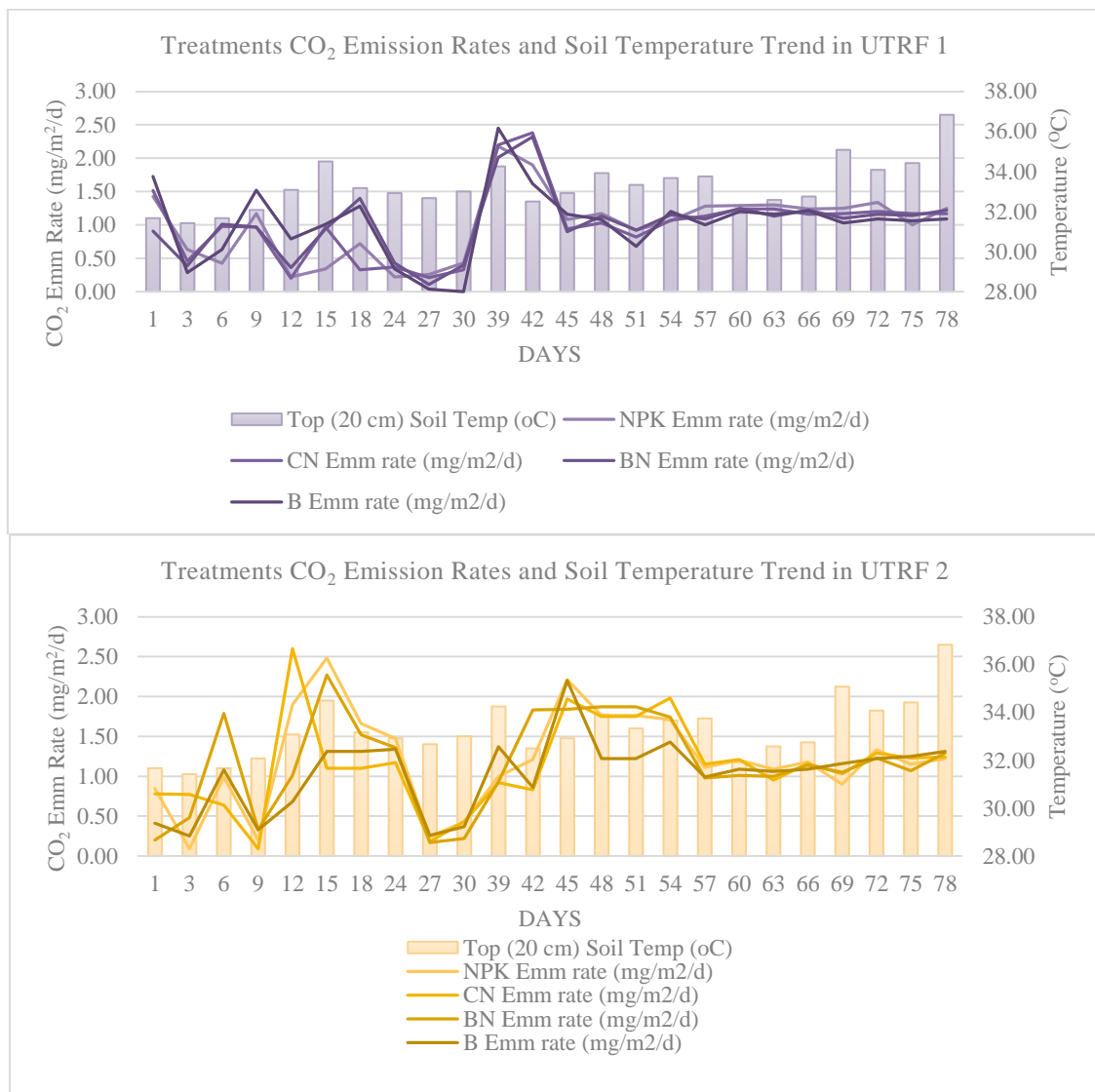


Fig. 2. Soil temperature and CO₂ emission rate trends in soils and treatments

Table 7. *CO₂ emission rate, rainfall and soil temperature relationships in soils and treatments*

Soil	Treatment		Rainfall (mm)	Top (20 cm) Soil Temp (°C)
	Emission Rate (mg m ⁻² d ⁻¹)			
UTRF 1	NPK	r	-.080	.040
		P	.711	.853
	C	r	.144	.059
		p	.503	.784
	BN	r	.110	.118
		P	.610	.582
	B	r	-.100	-.017
		P	.642	.939
UTRF 2	NPK	r	.170	.295
		P	.427	.161
	C	r	-.055	.287
		P	.797	.174
	BN	r	.323	.238
		P	.123	.263
	B	r	.211	.444*
		P	.323	.030

N=24, *. Correlation is significant at the 0.05 level (2-tailed), CN: control treatment; B: biochar treatment; NPK: NPK treatment; BN: biochar-NPK treatment

Table 8. *General CO₂ emission rate, rainfall and soil temperature relationships in experimental treatments*

Treatment		Top (20 cm) Soil Temp (°C)	Rainfall (mm)
B Emm rate (mg m ⁻² d ⁻¹)	R	0.289*	0.096
	P	0.046	0.516
BN Emm rate (mg m ⁻² d ⁻¹)	R	0.264	0.224
	P	0.070	0.127
C Emm rate (mg m ⁻² d ⁻¹)	R	0.216	0.058
	P	0.140	0.698
NPK Emm rate (mg m ⁻² d ⁻¹)	R	0.261	0.081
	P	0.074	0.586

N=24, *. Correlation is significant at the 0.05 level (2-tailed), CN: control treatment; B: biochar treatment; NPK: NPK treatment; BN: biochar-NPK treatment

Relationship Between Soil Moisture and C Mineralization in Soils and Treatments

Fig. 3 shows the trends of soil moisture and C mineralisation in this study. As with soil temperature, there was no strong consonance between soil moisture and C mineralisation fluctuations. This is reinforced by the correlation analysis carried out. The results showed that rainfall amount had no significant correlation with C mineralisation and CO₂ emissions under treatments in both soils. Also, the direction of relationships differed slightly between treatments, with NPK and B treatments having a weak negative correlation in UTRF 1 and the control (C) treatment in UTRF 2.

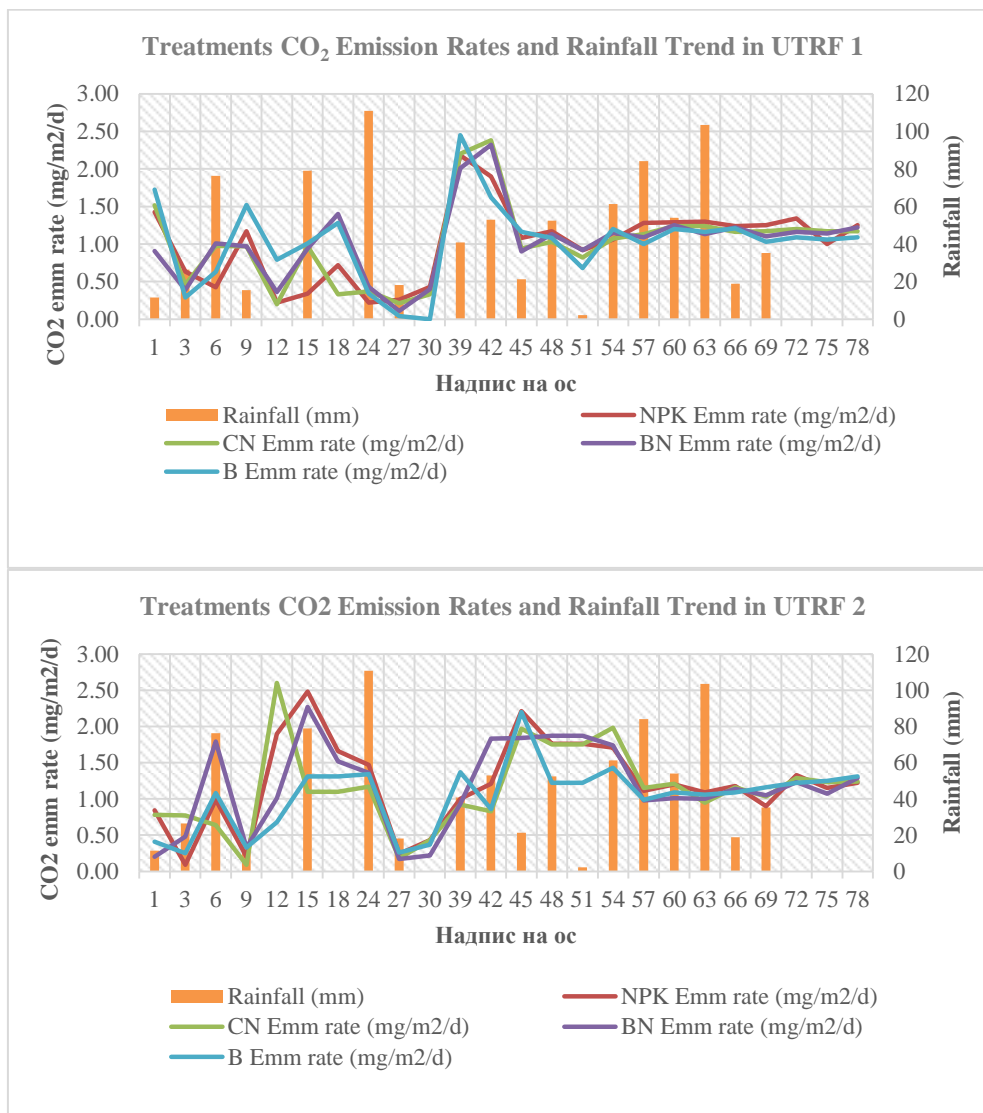


Fig. 3. Rainfall trend and treatments CO₂ emission rates in soils and treatments

This finding supports models that have shown that C mineralisation declines under elevated moisture. In their study, Benbi and Khosa (2014) found that the flooding of experimental soils reduced the mineralisation of added C. In a separate study, Huang and Hall (2017) reported an initial (25 days) suppression of C mineralisation, following water saturation above field capacity. However, after this initial period, they reported that elevated moisture stimulated cumulative CO₂ and CH₄ losses up to over 150 % compared to the

control. Stable C isotopes examination in their study showed that C losses were derived from C₃-C release under Fe reduction at high soil moistures.

The observations in this study suggest that soil C losses with soil water may be more connected to the leaching DOC. Studies have shown that moisture-induced high C mineralisation results in moisture levels that optimise soil oxygen supply and carbon substrate diffusion (Linn and Doran, 1984). As this study was carried out during peak rainfall in the study area, which results in high water saturation above field capacity, the saturating may have resulted in the C mineralisation observations recorded.

Conclusion and Recommendations

In examining the influence of soil management, temperature and moisture on C mineralisation in this study, the finding showed that assessed management options did not significantly affect C mineralisation. However, the two soils evaluated differed in C mineralisation responses. This observation could be attributed to a variation in soil properties, most likely OC, since the soils were mainly similar in other properties except in OC gradient. Findings showed that C mineralisation is more sensitive to soil temperature under sole biochar treatment. Although this observation did not cut across both soils studied individually, analyses showed that higher temperatures increased C mineralisation under exclusive biochar treatment. The outcome of this study can be applied in timing biochar application to the soil to maximise its carbon sequestration potential.

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References

- Ajadi, B.S., Adeniyi, A., Afolabi, M.T. (2011). Impact of climate on urban agriculture: Case study of Ilorin City, Nigeria. *Global Journal of Human Social Science*, 11(1), 24-29.
- American Society for Testing and Materials (ASTM) standard. (2009). Standard test method for chemical analysis of wood charcoal. Conshohocken, PA: American Society for Testing and Materials (ASTM) International.
- Benbi, D.K., Khosa, M.K. (2014). Effects of Temperature, Moisture, and Chemical Composition of Organic Substrates on C Mineralization in Soils. *Communications in Soil Science and Plant Analysis*, 45 (21) 2734-2753, DOI: 10.1080/00103624.2014.950423
- Blake, G.R., Hartage, K.H. (1986). Bulk Density, in: Klute, A. (Eds), *Methods of soil analysis part 1*, Madison, Wisconsin: American Society of Agronomy No. 9. pp. 365-375.
- Bray, R.H., Kurtz, L.T. (1945). Soil determination of total organic and available form of phosphate in soils. *Soil Science*, 59, 225-229. DOI:10.1097/00010694-194501000-00006
- Bremner, J.M. (1960). Determination of nitrogen in soil by the Kjeldahl method. *Journal of Agricultural Science*, 55, 11-31. DOI: 10.1017/S0021859600021572

- Ding, X., Yuan, Y., Liang, Y., Li, L. and Han, X. (2014). Impact of long-term application of manure, crop residue, and mineral fertiliser on organic carbon pools and crop yields in a Mollisol. *Journal of Soils Sediments*, 14, 854–859.
- El-Naggar, A., Lee, S.S., Awad, Y.M., Yang, X., Ryu, C., Rizwan, M., Rinklebe, J., Tsang, D.C.W. and Ok, Y.S. (2018). Influence of soil properties and feedstocks on biochar potential for carbon mineralisation and improvement of infertile soils. *Geoderma*, 332, 100–108. DOI:10.1016/j.geoderma.2018.06.017
- Enders, A. and Lehmann, J. (2012). Comparison of wet digestion and dry-ashing methods for total elemental analysis of biochar. *Communications in Soil Science and Plant Analysis*, 43, 1042–1052. DOI: 10.1080/00103624.2012.656167
- Gee, W.G., Or, D. (2002). Particle-size analysis, in: Dane, J., Topp, G.C. (Eds.), *Methods of Soil Analysis*, Book series: 5. Part 4. Soil Science Society of America, USA, pp 255–293.
- Guo, N., Shi, X., Zhao, Y., Xu, S., Wang, M., Zhang, G., Wu, J., Huang, B., Kong, C. (2017). Environmental and anthropogenic factors driving changes in paddy soil organic matter: A case study in the middle and lower Yangtze River Plain of China. *Pedosphere*, 27, 926–937.
- Haber, W. (1958). Ecological analysis of soil respiration (review of methods). *Flora*, 146, 109–157.
- Hackl, E., Pfeffer, M., Dona, C., Bachmann, G., Zechmeister-Boltenstern, S. (2005). Composition of the microbial communities in the mineral soil under different types of natural forest. *Soil Biology & Biochemistry*, 37, 661–671. DOI: 10.1016/j.soilbio.2004.08.023
- Herold, N., Schoening, I., Michalzik, B., Trumbore, S., Schrumpf, M. (2014). Controls on soil carbon storage and turnover in German landscapes. *Biogeochemistry*, 119, 435–451. DOI: 10.1007/s10533-014-9978-x
- Hopkins, D.W. (2006). Carbon Mineralisation, in: Carter, M.R. & Gregorich, E.G. (Eds.), *Soil sampling and methods of analysis*. Boca Raton, FL 33487-2742: Taylor & Francis Group, LLC. pp. 589–598.
- Huang, W., Hall, S.J. (2017). Elevated moisture stimulates carbon loss from mineral soils by releasing protected organic matter. *Nature Communications*, 8, 1774. DOI:10.1038/s41467-017-01998-z
- Jamala, G.Y. and Oke, D.O. (2013). Soil organic carbon fractions as affected by land use in the Southern Guinea Savanna Ecosystem of Adamawa State, Nigeria. *Journal of Science and Environmental Management*, 4(6), 116–122.
- Juo, A.R., Ayanlaja, S.A., Ogunwale, J.A. (1976). An evaluation of cation exchange capacity measurements for soils in the tropics. *Communications in Soil Science and Plant Analysis*, 7, 751–761. DOI: 10.1080/00103627609366684
- Kimetu, J.M., Lehmann, J., Kinyangi, J.M., Cheng, C.H., Thies, J., Mugendi, D.N., Pell, A. (2009). Soil organic C stabilisation and thresholds in C saturation. *Soil Biology & Biochemistry*, 41, 2100–2104. DOI:10.1016/j.soilbio.2009.07.022
- Linn, D.M., Doran, J.W. (1984). Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and non-tilled soils. *Soil Science Society of America Journal*, 48, 1267–1272. DOI: 10.1023/A:1015062304915
- Olaniyan, J.O., Isimikalu, T.O., Raji, B.A., Affinnih, K.O., Alasinrin, S.Y. and Ajala, O.N. (2020). An investigation of the effect of biochar application rates on CO₂ emissions in

soils under upland rice production in southern Guinea savannah of Nigeria. *Heliyon*. 6 (11), E05578, ISSN 2405-8440, DOI:10.1016/J.Heliyon.2020.E05578

Olaniyan, J.O., Ogunkunle., A.O. (2007). An evaluation of the soil map of Nigeria: II. Purity of mapping unit. *World Association of Soil and Water Conservation Journal*, 2, 97-108.

Parkin, T.B., Venterea, R.T. (2010). Chamber-Based Trace Gas Flux Measurements, in: Follet, RF (Eds.), *Sampling Protocols*. USDA-ARS. Pp 1-39. www.ars.usda.gov/research/GRACEnet

Peech, M., Cowan, R., Baker, G. (1962). A critical study of the BaCl₂-triethanolamine and the Ammonium acetate methods for determining the exchangeable hydrogen content of soils. *Soil Science Society of America Journal*, 26, 37-40. DOI:10.2136/sssaj1962.03615995002600010010x

Perveen, N., Ayub, M., Shahzad, T., Siddiq, M.R., Memon, M.S., Barot, S., Saeed, H., Xu, M. (2019). Soil carbon mineralisation in response to nitrogen enrichment in surface and subsurface layers in two land use types. *PeerJ*, 7, e7130, DOI:10.7717/peerj.7130

Renner, R. (2007). Rethinking biochar. *Environmental Science Technology*, 41, 5932-5933. PMID: 17937262, DOI: 10.1021/es0726097

Trivedi, P., Singh, B.P., Singh, B.K. (2018). Soil Carbon: Introduction, Importance, Status, Threat, and Mitigation, in: Singh, B.K., (Eds), *Soil Carbon Storage*. Academic Press, pp 1-28. ISBN 9780128127667, DOI:10.1016/B978-0-12-812766-7.00001-9

United States Department of Agriculture (USDA) Soil Science Division Staff. (2017). *Soil survey manual (Handbook 18 ed.)*. (C. Ditzler, K. Scheffe, & H. C. Monger, Eds.) Washington, DC: Government Printing Office.

United States Department of Agriculture (USDA) (2014). *Soil Survey Field and Laboratory Methods Manual*. Soil Survey Investigations Report No. 51 Version 2. (R. Burt, & S. S. Staff, Eds.) Lincoln, Nebraska: US Department of Agriculture, Natural Resources Conservation Service.

VandenBygaart, A.J., Gregorich, E.G. and Angers, D.A. (2003). Influence of agricultural management on soil organic carbon: a compendium and assessment of Canadian studies. *Canadian Journal of Soil Science*, 83, 363-380.

Walkley, A., Black, T. A. (1934). Organic matter determination. *Soil Science*, 37, 29-38.

Wang, Y., Cheng, S., Fang, H., Yu, G., Xu, X., Xu, M., Wang, L., Li, X., Si, G., Geng, J., He, S. (2015). Contrasting effects of ammonium and nitrate inputs on soil CO₂ emission in a subtropical coniferous plantation of southern China. *Biology & Fertility of Soils*, 51, 815-825. DOI: 10.1007/s00374-015-1028-x

Xiao, S., Wei, Z. and Kelin, W. (2017). Soil aggregate mediates the impact of land uses on organic carbon, total nitrogen and microbial activity in a karst ecosystem. *Soil Biology Biochemistry*, 21, 206-213.



Fertilizer-assisted Bioremediation of Sandy and Silty Clay Soils contaminated with Crude Oil

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Abstract

Crude oil contamination of farmlands and rivers has been a major concern in Nigeria, especially in places like Ogoni land in Rivers State and some other oil producing states. It has severely impacted on the economic and health status of people in that region. It is important to find ways to ameliorate the harmful effects of crude oil contamination on both terrestrial and aquatic lives. In this study, we investigated the bioremediation profile of sandy and silty clay soils contaminated with crude oil. Contaminated soils were treated with inorganic fertilizer (NPK 15:15:15) and urea to improve the density of soil microbes and enzymes. The total petroleum hydrocarbon (TPH), total heterotrophic bacteria (THB), total hydrocarbon utilizing bacteria (THUB), total heterotrophic fungi (THF), total hydrocarbon utilizing fungi (THUF), and the activities of soil enzymes such as laccase, peroxidase, lipase, and catalase were investigated. The results indicated that treatment of crude oil contaminated soils with NPK and urea increased the activities of soil enzymes and enhanced total soil microbial load that play active roles in biodegradation of petroleum products, thereby suggesting that NPK and urea treatments of soils have the potential of decreasing crude oil contamination and remediating contaminated soils. Furthermore, this study showed that NPK and urea decreased the total petroleum hydrocarbon (TPH) values of both sandy (92.5%) and silty clay (80.5%) soils. The findings from this study, suggest that NPK and urea application to contaminated soils could serve as beneficial remediation agents for quick mitigation of the hazardous effects of crude oil contamination on farmlands.

Keywords: Crude oil contamination, (Bio)remediation, Soil microbes and enzymes, NPK.

Introduction

Nigeria is one of the countries with large stores of crude oil, especially in the Southern part, and due to continuous oil drilling and exploration, there are many sites, including residential areas, farmlands, rivers, and the surrounding atmosphere that have been polluted. The pollution has affected both human and animal lives, through introduction of harmful petrochemical toxicants into the environment. The toxicants cause serious damage to various tissues and organs in the human body, terrestrial animals, and aquatic lives. Also, it affects farmlands and results in poor yield of agricultural products, and as a consequence lead to poor

economic status of the inhabitants. There are many petroleum industries that operate in the Southern part of Nigeria due to their rich oil store, and their operations, over the years, have led to the pollution of these territories and have rendered many of them uninhabitable. They have caused tremendous hardship to the communities and have affected the ecosystem adversely resulting in a loss of biodiversity (Akpofure et al., 2000). Oil spillage on farmlands usually reduces yields and destroys soil fertility until there is a proper clean-up of the farmland to restore the natural ecosystem processes and reestablish stability (Sada and Odemerho, 2000).

Different methods have been employed to remediate crude oil polluted sites, reduce the damage caused, and restore the natural processes that had been altered by the pollutants. Some of the methods include natural method, also known as natural attenuation; physical methods such as booming, skimming, washing, tilting, and sediment relocation; chemical methods such as the use of detergents, dispersants, de-emulsifiers, and surface film chemicals. Another viable method that has been applied in cleaning up polluted farmlands is bioremediation, which is a biological method. It is the use of biological agents which are capable of utilizing the toxic petrochemical agents as energy source, and in the process degrade them to non-toxic forms (USEPA, 1989).

Microorganisms and some plants have been reported as key players in the bioremediation processes. When plants are used to bioremediate a polluted soil, it is termed phytoremediation. Microorganisms such as bacteria and fungi that live ubiquitously and utilize large number of petrochemical compounds as energy source are essential agents in the bioremediation processes. They can degrade the contaminants and use them as source of energy because they are supplied with various enzymes that catalyze the breakdown of these compounds. Fungi produce extracellular enzymes directly unto the contaminants and degrade them to usable and less toxic forms which are then absorbed into the cells. In the case of bacteria, the contaminants are first absorbed into the cells before they are acted upon by the degrading enzymes. The combined action of fungi and bacteria results in a clean-up of the petrochemical toxicants and bioremediation of the polluted soils. Some of the degrading microorganisms that have been identified include *Aspergillus niger*, *Pseudomonas*, and *Penicillium* (Cooney, 1994). The supply of required nutrients to these microorganisms may enhance their bioremediation capacity of polluted soils. Therefore, in this study, crude oil-polluted soils were treated with NPK 15:15:15 and urea fertilizer as a way of supplying the resident microorganisms with nutrients to enhance their bioremediation capacity. Hence, the use of nutrients such as NPK and urea fertilizers on bioremediation of crude soils in the Niger-Delta region of Nigeria was investigated.

Materials and Methods

2.1. Collection of Soil Sample

Soil samples were collected from an unpolluted site in Nigeria. The soil samples were collected from a depth of 0-50 cm in a sterile polythene bag.

2.2. Determination of Physicochemical Properties

Two soil types (Sandy and Silt clay) were used for this study, and their physical and chemical properties were determined using reagents of analytical grade. The following were

the physicochemical properties determined: Available phosphorus, Total nitrogen, Total Organic Carbon (TOC), pH, bulk density, porosity, water holding capacity and electrical conductivity (EC). These properties were determined three days (0, 18, and 36 day).

2.3. Soil Temperature Measurement

A pilot hole was made in the soil using a screw driver, and the thermometer was inserted into the hole making sure it's firm and kept for several minutes until a stable temperature was achieved (Hewins et al., 2016). The temperature of the soil was taken at the site.

2.4. Soil pH Determination

The method of McLean (1982) was adopted. The soil was air-dried and 10 g was placed in a 25 mL beaker. Deionized water (10 mL) was then added to the soil sample and thoroughly mixed for 5 sec with glass rod, and the suspension was allowed to stand for 30 min. The pH was measured by inserting the electrode of calibrated pH meter into soil suspension.

2.5. Determination of Bulk Density

An empty universal bottle was weighed and filled with oven-dried soil sample up to the brim by tapping, and the weight was recorded. The volume of the bottle was determined using a burette (FAO, 1980), and the bulk density was calculated as follows:

$$\text{Soil Bulk Density (g/cm}^3\text{)} = \frac{\text{weight oven dry soil}}{\text{volume of soil}}$$

2.6. Determination of soil moisture content

Gravimetric method was used for this analysis (Reynolds, 1970). It involved the determination of mass difference between the wet soil and soil oven-dried at 105°C. An empty crucible was weighed and the mass was recorded as M_1 (g). the wet soil sample was positioned in a crucible and weighed immediately and the mass was recorded as M_2 (g). The crucible containing the wet sample was placed in an oven and dried at 105°C until a constant weight was achieved. The sample was removed from the oven and placed in a desiccator to cool. The crucible with the oven-dried soil was weighed and the mass was recorded was M_3 (g). The formular below was used to calculate moisture content:

$$\text{Moisture Content (\%)} = \frac{M_2 - M_3}{M_3 - M_1} \times 100$$

Where M_1 = Mass of empty crucible (g), M_2 = Mass of crucible and wet soil (g), M_3 = Mass of crucible and oven dried soil (g)

2.7. Water Holding Capacity of Soil

A small cup with perforated bottom was weighed and recorded. Filter paper was placed at the foot of the cup and the weight was taken. Soil sample (70 g) was then weighed into the cup on a retort stand and 250 mL measuring cylinder with funnel was inserted into it. Then, 50 mL of deionized water was added and it was allowed to drain overnight. The drained water was read and recorded (FAO, 1980). Water holding capacity of soil was calculated as follows:

$$\text{WHC} = \frac{\text{Volume of water retained}}{\text{Volume of sample}} \times 100$$

2.8. Soil Porosity

Air-dried soil was added to 500 mL measuring cylinder and 100 mL of deionized water was carefully and slowly added to the soil sample inside the measuring cylinder until it reached the top of the soil. The volume of water used was recorded (FAO, 1980), and porosity was calculated as follows:

$$\text{Porosity} = \frac{\text{Amount of water added to soil sample}}{\text{Total Soil Sample}} \times 100$$

$$(\text{Porosity } (\%) = 100 - (\text{bulk density/particle density}) \times 100)$$

2.9. Determination of Total Nitrogen in Soil

Soil sample (2 g) was weighed into an 800 mL Kjeldahl digestion flask, deionized water of 10 mL was added, followed by addition of 5 g of Kjeldahl catalyst mixture and 15 mL of 18.6 M sulphuric acid. The flask was cautiously heated on digestion stand until frothing stopped. The heat was increased until digest was clear, the flask was cooled and deionized water was slowly added and shaken. Three chips of granulated zinc were added and 30 mL of 2% boric acid were measured into 250 mL conical flask and placed under a condenser. Then, 75 mL of 10 M NaOH was slowly added into the digest in Kjeldahl flask and immediately connected to distillation apparatus. The distillate with NH_3 liberated was titrated with a standard acid along with four drops of mixed indicator (FAO, 1980). Total nitrogen was calculated as follows:

$$\text{Total Nitrogen } (\%N) = \frac{(\text{Equivalents of acid added to sample} - \text{equivalents of acid added to blank})(14.01)(100)}{\text{Sample weight (g)}}$$

2.10. Available Phosphorus in Soil

Air-dried soil (2.5 g) was placed in a clean and dried 125 mL polyethylene bottle, followed by the addition of 50 mL of 0.5 M sodium bicarbonate (pH 8.0) with polyacrylamide, which was used as the extracting solution from a dispenser. The bottle was placed in a reciprocating shaker and shook for 30 min and filtered into test tube with filter paper. Technicon II Autoanalyzer was used to determine the available phosphorus in clear filtrate by colorimeter. Soil phosphorus was calculated as:

$$\text{Soil Phosphorus (mg/kg)} = \frac{A \times B \times C \times M}{E}$$

Where, A = Sample extract reading (mg l⁻¹), B = Extract volume (ml), C = Dilution, if performed, M = Moisture correction factor, E = Sample weight (g)

2.11. Total Petroleum Hydrocarbon (TPH)

Sandy and silty clay soil samples (5 g) contaminated with 5000 ppm of crude oil or co-treated with NPK and urea at CPN ratio of 100:2:0:2 were extracted three times with 15 mL of hexane each. The three extracts (three) were pooled and dried by solvent evaporator at room temperature under gentle nitrogen stream in a fume hood. Residues were weighed along with solvent blank beaker. The difference of the weight was calculated as the total petroleum hydrocarbon content (Chandra et al., 2013).

2.12. Gas Chromatographic Analysis of Soil

Five grams (5 g) of the soil sample was mixed with 5 g of anhydrous sodium sulphate in a 25 mL vial, 15 mL of n-hexane was added and vortexed for 10 min. The resulting soil suspension was filtered using a 0.45 µm Teflon filter. The filtrate was analyzed using a gas chromatography with flame ionization detector (GC-FID) (HP 7890). The injector and detector temperatures were programmed at 250°C and 350°C, respectively. The initial oven temperature was maintained at 50°C, ramped at a rate of 5 - 280°C per min, and held for 6 min. The injection volume for both sample and standards were 1 µL.

2.13. Soil Enzymes Assays

2.13.1. Laccase Activity

Laccase activity was determined using pyrogallol as substrate (Allison and Jastrow, 2006). Briefly, 1 g of soil sample was weighed into a 250 mL conical flask and 50 mL acetate buffer (50 mM, pH 5.0) was added. The flask was incubated at room temperature for 1 h with vigorous shaking every 20 min. The volume of the buffer was increased to 125 mL and the flask shaken vigorously. Aliquot of 10 mL of the soil suspension was transferred to a centrifuge tube and centrifuged at 4000 rpm for 10 min. The supernatant obtained was used for the enzyme assay. The test experiment contained 2 mL of the supernatant (soil suspension) and 1 mL substrate (25 mM pyrogallol). This was incubated in the dark at room temperature for 1 h. A sample control containing 2 mL supernatant and 1 mL buffer and also substrate control containing 1 mL substrate and 2 mL buffer were treated as the test experiment. The absorbance was measured at 460 nm using UV – Visible spectrophotometer. The buffer solution was used as blank. Laccase activity was calculated as follows:

$$\text{Laccase activity } (\mu\text{mol/h/g}) = \frac{A \times V_1}{E \times V_2 \times T \times W}$$

Where, *A* = Net absorbance = Test – sample control – substrate control, *V*₁ = Volume of buffer used, *E* = Molar extinction coefficient for pyrogallol = 4.2/µmol, *V*₂ = Volume of soil suspension, *T* = Substrate incubation time, *W* = Mass of soil sample

2.13.2. Peroxidase Activity

Peroxidase activity was estimated using pyrogallol as substrate (Allison and Jastrow, 2006). The procedure described for laccase activity was followed, but with the addition of 0.2 mL of 0.3% hydrogen peroxide to the test, sample control and substrate control experiments respectively.

2.13.3. Lipase Activity

Lipase activity was determined using the method described by Parry et al (1966). Briefly, 1 g of soil sample was weighed into a 250 mL conical flask and 100 mL phosphate buffer (50 mM, pH 7.4) was added. The conical flask was shaken vigorously and then incubated at room temperature for 1 h with intermittent shaking. Thereafter, 10 mL of the soil suspension was transferred to a centrifuge tube and centrifuged at 4000 rpm for 10 min. The supernatant was used for the lipase activity assay. The test experiment was made up of 1 mL supernatant and 5 mL 10% olive oil and gum Arabic emulsion in a conical flask. The flask was incubated for 1 h on a shaker with the speed adjusted to high and temperature set at 40°C. At the end of the incubation, 1 mL 95% ethanol was added to the conical flask and shaken to stop the reaction. The free fatty acid released was determined using a UV spectrophotometer. Control experiment was also one with 1 mL buffer solution.

Lipase activity was calculated as follows:

$$\text{Lipase activity (U/g)} = \frac{(V_S - V_B) \times N \times 1000}{S}$$

Where V_B = Volume of NaOH used against control flask, V_S = volume of NaOH used against experimental flask, N = Normality of NaOH, S = Volume of enzyme extract,

2.13.4. Catalase Activity

Catalase activity was determined according to the method of Cohen et al (1970). Briefly, soil sample supernatant was obtained as described for lipase activity. The supernatant (1 mL) was transferred to a test tube and 5 mL of 0.3% hydrogen peroxide was added. The content of the test tube was mixed by shaking and was then incubated at room temperature for 5 min. The reaction was stopped by the addition of 1 mL of 6 N sulphuric acid and 0.01 M KMnO_4 was added within 3 sec. The absorbance was measured using a spectrophotometer at 480 nm within 30-60 sec. Control experiment was performed using deionized water. Catalase activity was calculated as follows:

$$\text{Catalase activity (U/g)} = \frac{\left(\frac{\text{Absorbance}}{t}\right) \times V \times 1000}{M \times v \times W}$$

Where, Absorbance = absorbance (control) – absorbance (test), V = total volume of reaction mixture, M = molar extinction coefficient = 40.0, v = volume of supernatant used, W = mass of soil sample, t = reaction incubation time = 5 min.

2.14. Effect of Abiotic Treatment on Crude Oil Biodegradation in Soil

The ex-situ remediation method of Saterbak et al (2000) was adopted with modification. Briefly, each soil sample (3 kg) contaminated with crude oil (3000, 5000, and 8000 mg/kg) was weighed into 7 plastic buckets for each soil type (sandy soil and silty clay). Moisture content (MC) was adjusted to 60-80% of water holding capacity (WHC) for all group. Each container was agitated every three days and same with moisture adjustment. The experiment lasted for 36 days with the following determinations done every 6 days: Microbial growth were analyzed using, THB, THUB, THF, and THUF as markers.

2.15. Statistical Analysis

Experimental data were analyzed using IBM SPSS statistics 23 software for Windows. All data are expressed as mean \pm SEM (standard error of mean). ANOVA was used in comparing the mean followed by Duncan's Multiple Range (DMRT), Post Hoc test. Student's t test was used to compare means when only two means were involved. Statistical significance was taken as $p < 0.05$. Correlation analysis was done to establish relationship between TPH and the other parameters evaluated (THUF, THF, THB, THUB, laccase, peroxidase, catalase, lipase activities) respectively.

Results

3.1. Physicochemical Properties of Silty Clay and Sandy Soils Contaminated with Crude Oil

The results below show the physical and chemical properties of crude oil-contaminated sandy soil and silt clay.

Table 1. *Physicochemical data on silty clay and sandy soils contaminated with crude oil. Values are expressed as mean \pm SEM ($n = 3$, at 0, 18, and 36 day).*

Parameters	Silty clay contaminated				Sandy soil contaminated			
	Control	3000 ppm	5000 ppm	8000 ppm	Control	3000 ppm	5000 ppm	8000 ppm
pH	6.84 \pm 0.05	5.70 \pm 0.01	5.50 \pm 0.04	5.70 \pm 0.03	6.33 \pm 0.31	6.71 \pm 0.13	6.51 \pm 0.36	6.80 \pm 0.63
Total nitrogen (mg/kg)	0.49 \pm 0.00	0.18 \pm 0.03	0.22 \pm 0.01	0.27 \pm 0.49	0.43 \pm 0.76	0.17 \pm 0.51	0.21 \pm 0.11	0.22 \pm 0.11
Available phosphorus (mg/kg)	7.10 \pm 2.38	4.42 \pm 1.10	4.48 \pm 1.15	4.53 \pm 2.20	6.10 \pm 2.09	3.42 \pm 1.25	3.48 \pm 1.32	3.53 \pm 1.10
TOC (%)	0.07 \pm 0.4	0.104 \pm 0.2	0.21 \pm 0.21	0.43 \pm 0.12	0.06 \pm 0.16	0.10 \pm 0.12	0.29 \pm 0.01	0.43 \pm 0.19
Potassium	8.91 \pm 2.01	6.55 \pm 1.98	6.59 \pm 1.52	6.61 \pm 1.31	6.93 \pm 1.65	4.54 \pm 1.11	4.57 \pm 1.21	4.59 \pm 1.41
TPH (mg/kg)	<1	7568	7601	7608	<1	7568	7601	7608
Moisture content (%)	0.30 \pm 0.02	0.32 \pm 0.04	0.74 \pm 0.01	1.32 \pm 0.05	0.25 \pm 0.08	0.28 \pm 0.01	0.69 \pm 0.03	1.27 \pm 0.06
Soil bulk density (g/cm ³)	1.09 \pm 0.02	2.87 \pm 0.12	2.92 \pm 0.15	2.02 \pm 0.98	1.69 \pm 0.76	2.81 \pm 0.23	3.94 \pm 0.31	4.08 \pm 0.68
Conductivity (μ S/cm)	180 \pm 3.10	190 \pm 2.87	170 \pm 1.99	190 \pm 2.55	160 \pm 2.20	170 \pm 2.01	150 \pm 1.89	170 \pm 1.77
Porosity	0.51 \pm 0.04	0.36 \pm 0.07	0.31 \pm 0.04	0.29 \pm 0.07	0.31 \pm 0.02	0.33 \pm 0.01	0.36 \pm 0.09	0.39 \pm 0.07
Water holding capacity	0.19 \pm 0.00	0.19 \pm 0.01	0.19 \pm 0.01	0.19 \pm 0.01	0.16 \pm 0.03	0.16 \pm 0.02	0.16 \pm 0.03	0.16 \pm 0.02
Temperature $^{\circ}$ C	27							
Particle size distribution								
* Silty clay %	72.1							
* Sand %	93							

3.2. Physicochemical Properties of Contaminated Silty Clay and Sandy Soils Treated with NPK and Urea Fertilizers.

The results below show the physical and chemical properties of contaminated sandy soil and silty clay treated with NPK 15:15:15 and urea at a CNP (carbon, nitrogen, and phosphorus) ratio of 100:2:0:2.

Table 2. *Impact of NPK and urea fertilizers on the physicochemical properties of silty clay and sandy soils contaminated with crude oil. Values are expressed as mean \pm SEM (n = 3, at 0, 18, and 36 day).*

Parameters		Treated silty clay			Treated sandy soil		
		3000 ppm	5000 ppm	8000 ppm	3000 ppm	5000 ppm	8000 ppm
pH		5.69±0.31	6.18±0.33	6.44±0.10	8.36±0.21	8.28±0.19	8.44±0.23
Total Nitrogen (mg/kg)		0.31±0.01	0.37±0.04	0.42±0.02	0.28±0.11	0.31±0.12	0.39±0.22
Available Phosphorus (mg/kg)		6.19±1.09	6.38±1.23	6.77±1.32	5.14±0.98	5.33±0.87	5.74±0.92
TOC %		1.26±0.21	2.02±0.12	4.48±0.31	1.26±0.23	2.02±0.22	4.48±0.31
Potassium		72.4±4.01	73.5±3.81	74.8±3.17	70.6±2.12	71.4±2.02	72.1±1.87
THC (mg/kg)		634±3.02	619±3.41	540±3.44	634±3.11	619±2.45	540±3.65
Moisture content (%)		3.81±0.33	3.93±0.23	4.02±0.31	3.76±0.43	3.88±0.14	3.97±0.22
Soil bulk density (g/cm³)		3.17±0.12	3.28±0.22	3.39±0.12	3.72±0.19	3.86±0.21	3.91±0.32
Conductivity (µs/cm)		230±4.40	200±3.98	228±3.99	210±3.01	180±3.41	208±3.06
Porosity		0.24±0.01	0.34±0.02	0.35±0.01	0.42±0.04	0.44±0.02	0.43±0.01
Water Holding Capacity		1.24±0.15	1.24±0.57	1.26±0.43	1.22±0.34	1.22±0.32	1.24±0.48
Temperature °C	26				27		
Particle Size Distribution							
*Silty clay (%)		72.1					
*Sandy soil (%)		93					

3.3. Effect of NPK and Urea on Soil Enzymes Activity

To investigate the effect of NPK and urea fertilizer treatment on enzymes activities of contaminated soils. Two different soil types, silty clay and sandy, contaminated with crude oil, were treated with NPK and urea fertilizers. The results indicated that the activities of soil enzymes were affected by applied treatment during the 36 days period. An increased activity was observed for laccase from days 0-18 on both soil types across the treated groups. However, laccase activity in sandy soil was higher compared to that of silty clay (Fig. 1.A). Peroxidase activity increased in 12 days from the start of the experiment across treated groups in both soils. Peroxidase activity in silty clay was higher than that of sandy soil (Fig. 1.B). Furthermore, an increased activity was recorded for catalase in sandy soil and silty clay with the highest peak at day 18. Catalase activity in sandy soil was higher than that of silty clay (Fig. 1.C). Also, lipase activity increased from days 0-12 in sandy soil while for silty clay, the highest activity was on day 24 (Fig. 1.D). Taken together, these results suggested that treatment of crude oil contaminated soils with NPK and urea fertilizers has the potential of enhancing soil enzymes activity that function in degrading crude oil contaminant.

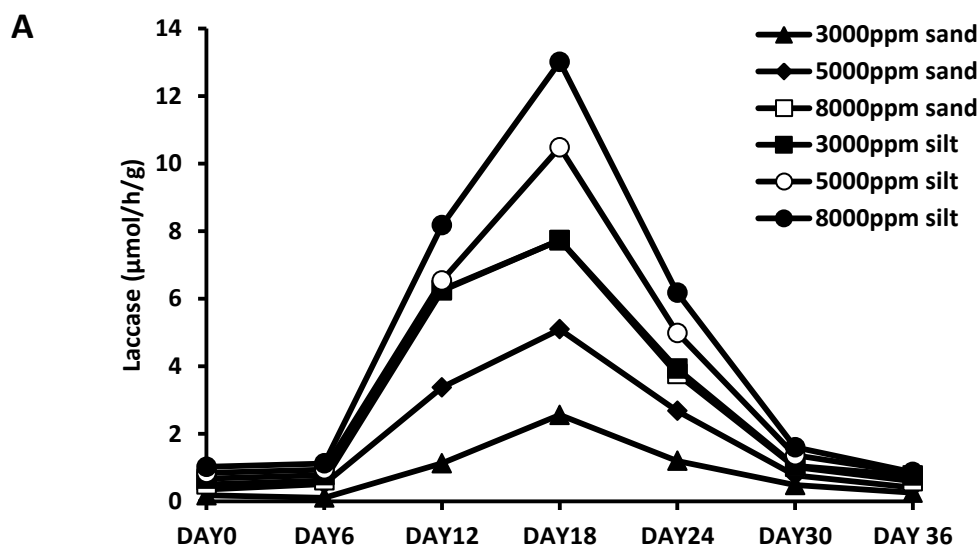


Fig. 1. (A) Effect of NPK and urea fertilizers on soil enzymes activities. Effect of NPK and urea on soil laccase activity. Values are expressed as mean \pm SEM ($n = 3$). $P < 0.05$.

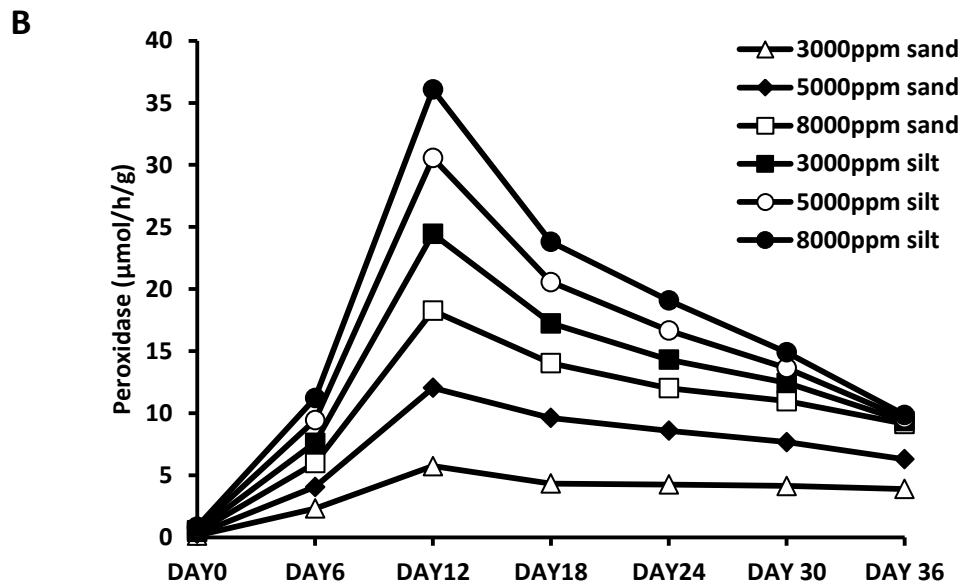


Fig. 1. (B) Effect of NPK and urea fertilizers on soil enzymes activities - Effect of NPK and urea on soil peroxidase activity. Values are expressed as mean \pm SEM ($n = 3$). $P < 0.05$.

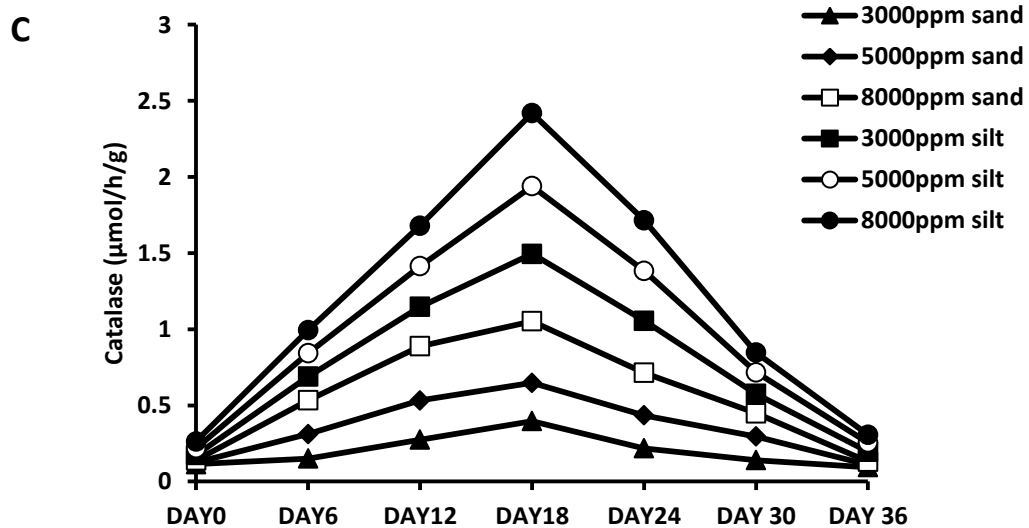


Fig. 1. (C) Effect of NPK and urea fertilizers on soil enzymes activities. Effect of NPK and urea on soil catalase activity. Values are expressed as mean \pm SEM ($n = 3$). $P < 0.05$.

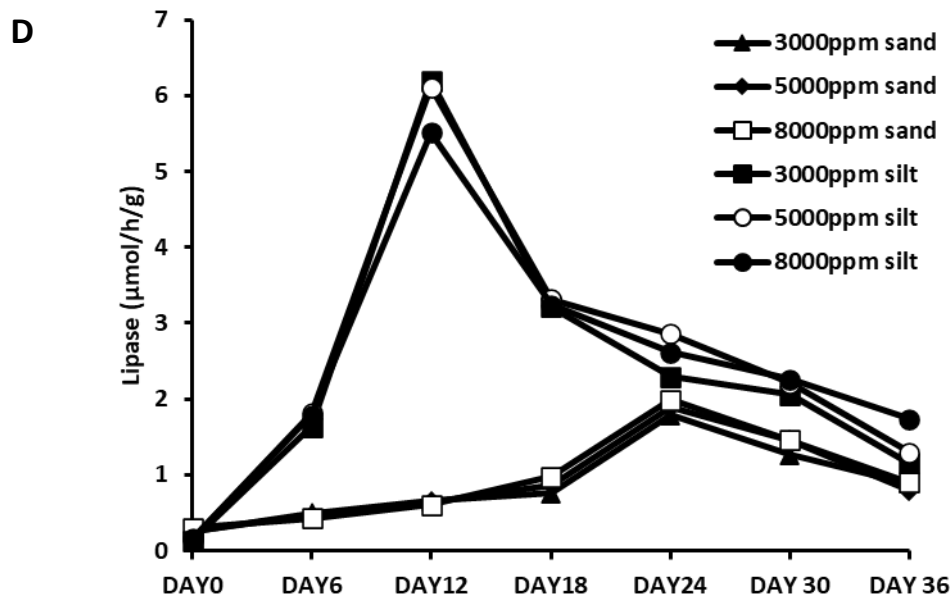


Fig. 1. (D) Effect of NPK and urea fertilizers on soil enzymes activities. Effect of NPK and urea on soil lipase activity. Values are expressed as mean \pm SEM ($n = 3$). $P < 0.05$.

3.4. Effect of NPK and Urea Treatment on Soil Microbial Load

To investigate the effect of NPK and urea fertilizers on soil microbial load. Sandy and silty clay soils were treated with NPK 15:15:15 and urea, and the microbial load was monitored and reported as CFU/g during the 36 days period of treatment. An increase in amount of total hydrocarbon utilizing fungi (THUF) and total heterotrophic fungi (THF) were observed from day 0 and peaked on day 12 for both sandy and silty clay soils before decreasing thereafter in all the treatments (Fig. 2.A and B). The same pattern of growth was observed for total hydrocarbon utilizing fungi (THUB) and total heterotrophic fungi (THB) with maximum peak on day 18 (Fig. 2.C and D). These results indicated that treatment of crude oil contaminated soils with NPK and urea fertilizers enhanced the total soil microbial load. Increased soil microbial load results in increased degradation of crude oil contaminant in the soils and hence helps to ameliorate the toxic effects of crude oil on soils.

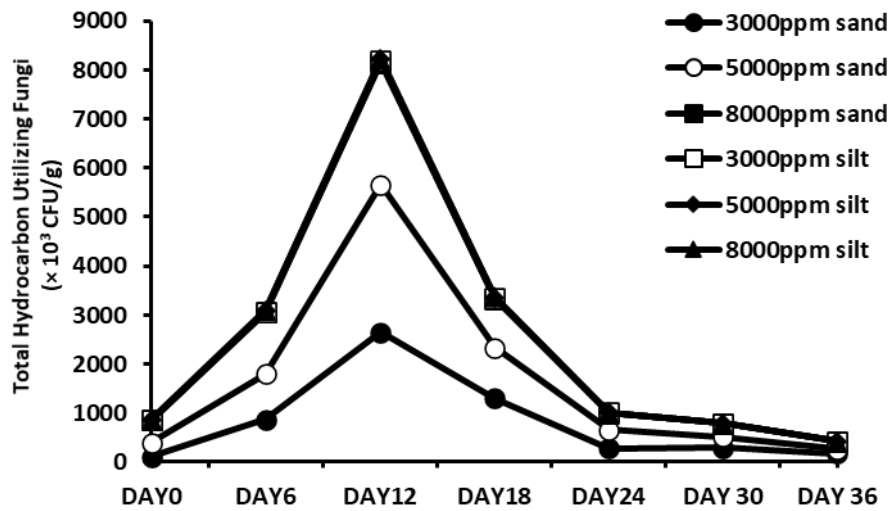
A

Fig. 2. (A) Effect of NPK and urea on soil microbial load of soil contaminated with crude oil. Effect of NPK and urea on THUF of sandy and silty clay soils. Values are expressed as mean \pm SEM ($n = 3$). $P < 0.05$.

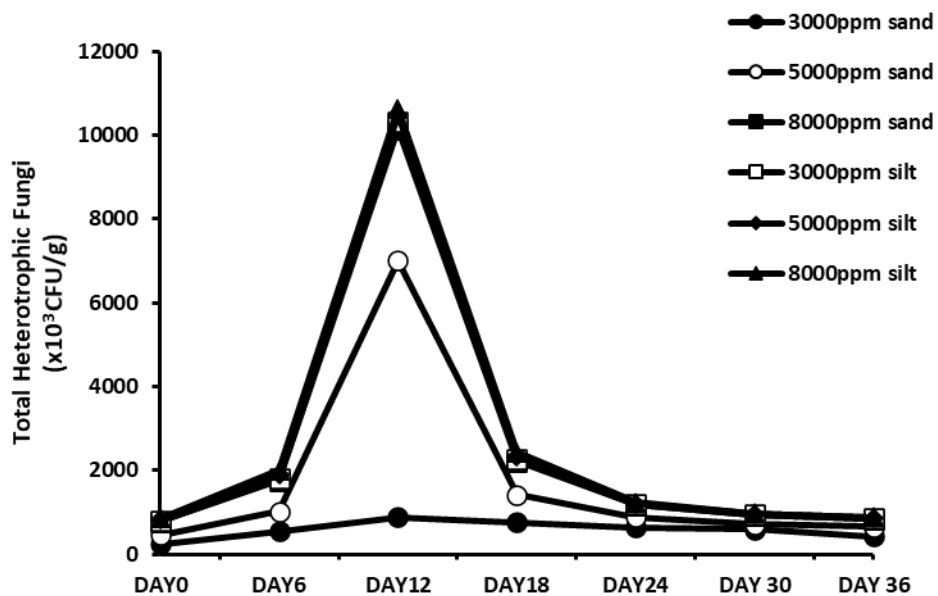
B

Fig. 2. (B) Effect of NPK and urea on soil microbial load of soil contaminated with crude oil. Effect of NPK and urea on THF of sandy and silty clay soils. Values are expressed as mean \pm SEM ($n = 3$). $P < 0.05$.

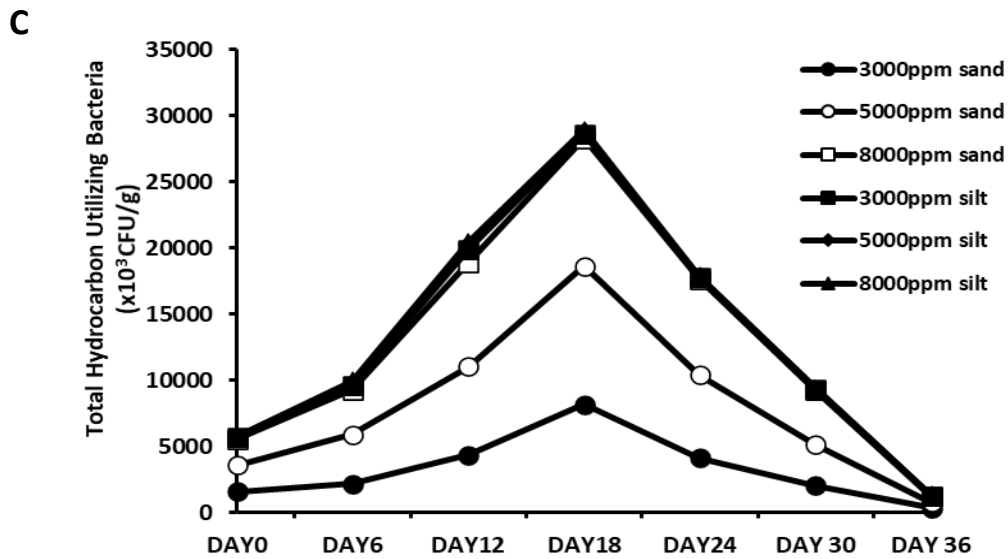


Fig. 2. (C) Effect of NPK and urea on soil microbial load of soil contaminated with crude oil. Effect of NPK and urea on THUB of sandy and silty clay soils. Values are expressed as mean \pm SEM ($n = 3$). $P < 0.05$.

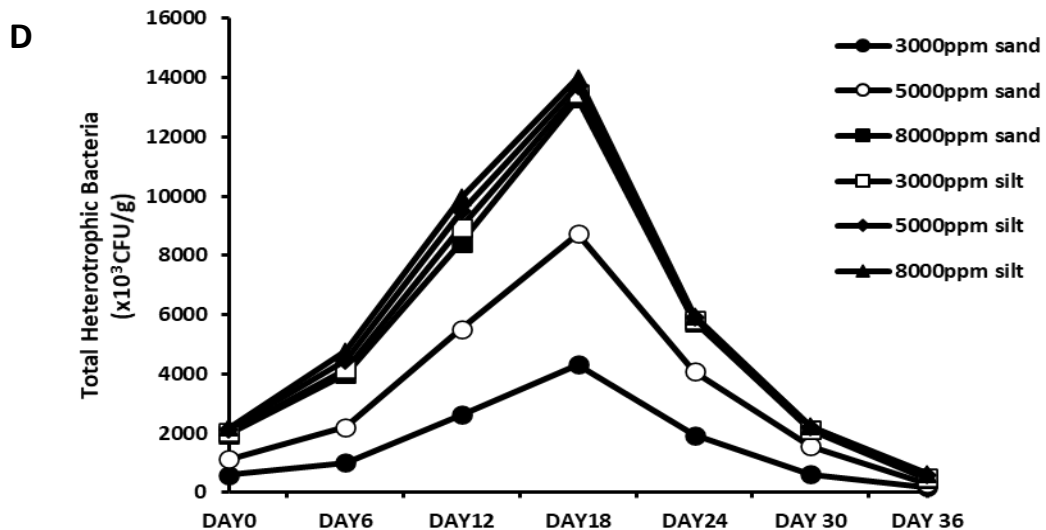


Fig. 2. (D) Effect of NPK and urea on soil microbial load of soil contaminated with crude oil. Effect of NPK and urea on THB of sandy and silty clay soils. Values are expressed as mean \pm SEM ($n = 3$). $P < 0.05$.

3.5. Effect of NPK and Urea Treatment on Total Petroleum Hydrocarbon

The effect of NPK and urea fertilizers on oil degradation at 5000 ppm on sandy soil and silty clay was investigated. A significant decrease in total petroleum hydrocarbon (TPH) concentration was observed in both soil types. Comparatively, the rate of TPH reduction in sandy soil was higher than that of silty clay as the former having 92.90% TPH reduction and the latter having 80.46% after the 36 days enhanced treatment.

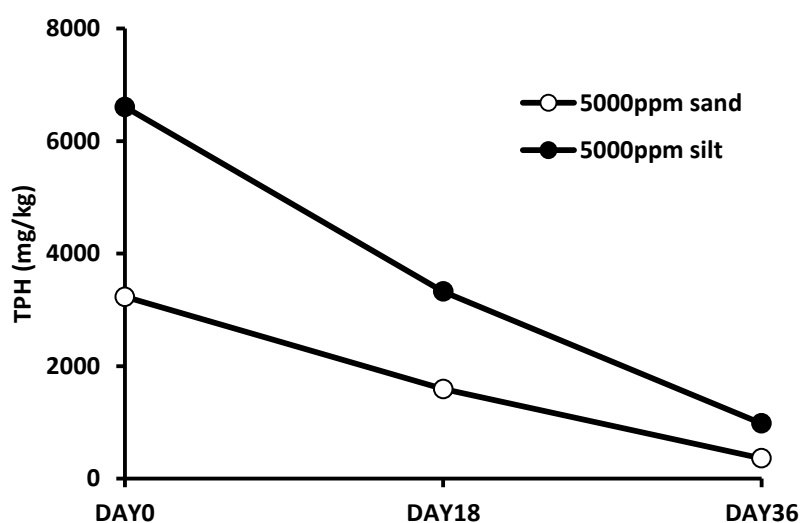


Fig. 3. Effect of NPK and urea on TPH of soils contaminated with crude oil. Values are expressed as mean \pm SEM ($n = 3$). $P < 0.05$.

Discussion

Petrochemical discharge from crude oil industries on farmlands is one of the major problems faced by some parts of Nigeria. These petroleum products are harmful to body tissues and organs resulting in life-threatening disease conditions. Plants and aquatic lives are affected as well by the toxic nature of these substances. Therefore, there is an urgent need to clean up the pollution to restore normalcy of the ecosystem. This study investigated the additional effects of nutrients, in the form of NPK and urea fertilizers, on the bioremediation of crude oil-polluted soils. The results indicated that crude oil polluted soils had higher electrical conductivity, bulk density, and water holding capacity as compared to the unpolluted soil. This was in agreement with the report of other investigators (Barua et al., 2011). However, other properties as pH, total organic carbon, potassium, moisture content, and phosphorus were higher in the uncontaminated soil compared to the contaminated sample (Table 1 and 2). Crude oil in the soil is known to affect the properties and productivity of soil (Bosma et al., 1997; Michel and Fingas, 2016). The sandy nature, porosity and the pH of the contaminated soil supports leaching and possible contamination of the ground water (Bosma et al., 1997; Michel and Fingas, 2016). Inorganic nutrient sources like NPK 15:15:15 and urea

with nitrogen content of 46.6% was used in this study, because the quantification of required nutrient level in bioremediation studies is easier when inorganic nutrients are used (Suja et al., 2014; Shahi and Aydin, 2016).

Laccase and peroxidase are key extracellular oxidative enzymes produced by oleophilic microbes (Bach et al., 2013; Godoy et al., 2016). They were assayed in this study and a negative relationship was established between them (oxidative enzymes activity) and TPH using Pearson correlation. This indicated that increase in oxidative enzyme activity corresponded with decrease in TPH in soils (Fig. 1.A and B). However, the correlation between enzyme activity and microbial load was significant and positive indicating a corresponding increase of both enzyme activity and microbial load during the degradation process in both sandy soil and silt clay. The activities of catalase and lipase were used to monitor the reduction in toxicity level following oil degradation in soil (Margesin and Zimmerbauer, 1999; Riffaldi et al., 2006; Mahmoud et al., 2016), because they provide useful information about the soil quality. There was an increase in activity of both catalase and lipase in all treated variants. Catalase activity in soil decreased with increasing oil concentration (Fig. 1c). Wu et al (2016) corroborated this finding and affirmed the suitability of catalase activity for monitoring the bioremediation of crude oil. Other researchers including Achuba and Peretiemo-Carke (2008), Ajao et al (2011), and Achuba and Okoh (2014) have all reported increase in catalase activity during bioremediation as a mark of increased microbial activity. Similar result was observed in this study when catalase activity was monitored in treated sandy soil and silty clay. Lipase catalyzes the hydrolysis of glycerides at water-lipid interface to enable the hydrolysis products of lipids to be absorbed and used for metabolic activities by the microbes (Margesin and Zimmerbauer, 1999; Mahmoud et al., 2016). It was used by Margesin and Schinner (2001) to monitor the degradation of hydrocarbon in the soil. This study showed a decrease in lipase activity of contaminated soil (Fig. 1.C and D), but the activity increased in the treated variants. This result is in agreement with the report of other researchers who also reported a negative correlation of lipase activity and reduction in TPH (Margesin and Schinner, 2001). Achieving the desired CNP ratio is an important consideration in bioremediation optimization (Bach et al., 2013). Microbial activity could be inhibited when limiting nutrients are supplied at high concentration to the bioremediation system, hence it is important to measure the optimum CNP ratio (Huesemann, 1994). The CNP ratio of 100:10:1 has been reported to be the optimum ratio for oil bioremediation in soil (Huesemann, 1994; Wu et al., 2016). In this study, we recorded $92.95 \pm 0.02\%$ for sandy soil and $80.46 \pm 0.0311\%$ for silty clay degradation with CNP ratio of 100:2:0.2 after 36 days (Fig. 2). This indicated that there was a high reduction in TPH for both soils. The treatments increased soil microbial load monitored by THB, THUB, THF, THUF analysis (Fig. 3). Increase in the bacterial load was rapid from days 0-18 like the increase in fungal load from days 0-12.

The bioremediation was successful in both sandy and silty clay soils with 93% and 80.5% degradation of TPH respectively (Fig. 3). However, the reason for the lower TPH degradation rate in silty clay soil than sandy soil could be due to inefficient oxygen transfer in the soil. Fine grained clay with high surface area formed a sticky texture in the presence of water, blocking efficient oxygen transfer through the soil. Sandy soil on the other hand is more porous than silty clay. Higher porosity allows better oxygen transfer in the soil which is

essential to biodegradation of hydrocarbon. Larger pores also provide enough space for microbial growth. It has been demonstrated that pores smaller than 3 μm are not accessible to bacteria (Aislabie and Deslippe, 2013).

Another reason for low degradation of hydrocarbon in silty clay could be strong adsorption of the pollutant on the surface of soil particles. For the treated sandy soil, the crude oil residue on the 36th day of bioremediation was 362.5 mg/kg while that of silty clay was 418.5 mg/kg on day 36, indicating that oil remediation in sandy soil was faster compared to silt clay.

Conclusion

Crude oil pollution of soil has become recurrent in Nigeria with little or no solution due to over dependence on oil as the main source of revenue for the country. Therefore, considering the negative impact on the ecosystem, bioremediation techniques which include the use of fertilizers such as NPK and urea, in amounts that will not further compound the environmental and climate change problems, is highly recommended.

References

- Achuba, F.I., Okoh, P.N. (2014). Effect of petroleum products on soil catalase and dehydrogenase activities. *Open Journal of Soil Science*, 4, 399-406.
- Achuba, F.I., Peretiemo-Clarke, B.O. (2008). Effect of spent engine oil on soil catalase and dehydrogenase activities. *International Agrophysics*, 22, 1-4.
- Aislabie, J., Deslippe, J.R. (2013). *Soil microbes and their contribution to soil services*, J.R Dymond edition., Manaaki Whenna Press, Lincoln, New Zealand.
- Ajao, A.T., Oluwajobi, A.O., Olatayo, V.S. (2011). Bioremediation of soil microcosms from auto-mechanic workshops. *Journal of Applied Sciences and Environmental Management*, 15, 473-7.
- Akpofure, E.A., Efere, M.L., Ayawei, P. (2000). *The adverse effects of crude oil spills in the Niger Delta*, Urhobo Historical Society, 1, 21-33.
- Allison, S.D., Jastrow, J.D. (2006). Activities of extracellular enzymes in physically isolated fractions of restored grassland soil. *Soil Biology and Biochemistry*, 38, 3245-56.
- Bach, C.E., Warnock, D.D., Van Horn, D.J., Weintraub, M.N., Sinsabaugh, R.L., Allison, S.D., German, D.P. (2013). Measuring phenol oxidase and peroxidase activities with pyrogallol, L-DOPA and ABTS: Effect of assay conditions and soil types. *Soil Biology and Biochemistry*, 67, 183-91.
- Barua, D., Buragohain, J., Sarma, S.K. (2011). Certain physic-chemical changes in the soil brought about by contamination of crude oil in two oil fields of Assam, NE India. *European Journal of Experimental Biology*, 1, 154-61.
- Bosma, T.N.P., Middelorp, P.J.M., Schraa, G., Zehnder, A.J.B. (1997). Mass transfer limitation of biotransformation: quantifying bioavailability. *Environmental Science and Technology*, 31, 248-52.
- Chandra, S., Sharma, R., Singh, K., Sharma, A. (2013). Application of bioremediation technology in the environment contaminated with petroleum hydrocarbon. *Annals of Microbiology*, 63 (2), 417-31.

Cohen, G., Dembiec, D., Marcus, J. (1970). Measurement of catalase activity in tissue extracts. *Analytical Biochemistry*, 34, 30-8.

Cooney, J.J. (1994). The fate of petroleum pollutants in freshwater ecosystem, R.M. Atlas edition. *Petroleum microbiology*, Macmillan Publishing Co., New York.

Food and Agriculture Organization- FAO (1980). Soil testing and plant analysis: a basis for fertilizer recommendation. *FAO soil bulletin*, 38/2, FAO, Rome, Italy.

Godoy, P., Reiana, R., Calderon, A., Wittich, R.M., Garcia-Romera, I., Aranda, E. (2016). Exploring the potential of fungi isolated from PAH-polluted soil as a source of xenobiotics-degrading fungi. *Environmental Science and Pollution Research*, 23, 20986-96.

Hewins, D.B., Chuan, X., Bork, E.W., Carylyle, C.N. (2016). Measuring the effect of freezing on hydrolytic and oxidative extracellular enzyme activities associated with plant litter decomposition. *Pedobiologia*, 59, 253-6.

Huesemann, M.H. (1994). Guidelines for land-treating petroleum hydrocarbon-contaminated soil. *Journal of Soil Contamination*, 3, 299-318.

Mahmoud, B.M., Koutb, M.M.M., Morsy, F.M., Bagy, M.M.K. (2015). Characterization of lipase enzyme produced by hydrocarbon utilizing fungus *Aspergillus terreus*. *European Journal of Biological Research*, 5, 70-7.

Margesin, R., Schinner, F. (2001). Biodegradation and bioremediation of hydrocarbons in extreme environments. *Applied Microbiology and Biotechnology*, 56, 650-63.

Margesin, R., Zimmerbauer, A., Schinner, F. (1999). Soil lipase activity- a useful indicator of soil biodegradation. *Biotechnology Techniques*, 13, 313-33.

McLean, E.O. (1982). Soil pH and lime requirement, In page, A.L., R.H. Miller and D.R. Keeney (eds.). *Methods of soil analysis. Part 2- chemical and microbiological properties* (2nd edition). *Agronomy*, 9, 199-223.

Michel, J., Fingas, M. (2016). Oil spill causes, consequences, prevention and counter measures, G.M. Crawley ed., *Fossil fuels*, World Scientific Publishers.

Parry, R.M., Chandan, R.C., Shahani, K.M. (1966). Rapid and sensitive assay for milk lipase. *Journal of Dairy Science*, 49, 356-60.

Reynolds, S.G. (1970). The gravimetric method of soil mixture determination. *Journal of Hydrology*, 11, 258-73.

Riffaldi, R., Levi-Minzi, R., Cardelli, R., Palumbo, S., Saviozzi, A. (2006). Soil biological activities in monitoring the bioremediation of diesel oil-contaminated soil. *Water, Air, and Soil Pollution*, 170, 3-15.

Sada, P.O., Odemerho, F.O. (2000). *Environmental issues and management in Nigerian development*, fourth edition, Evans Brothers, Ibadan.

Saterbak, A., Toy, R.J., Mc Main, B.J., Williams, M.P., Dorn, P.B. (2000). Ecotoxicological and analytical assessment of effects of bioremediation on hydrocarbon-containing soils. *Environmental Toxicology of Chemistry*, 19, 2643-52.

Shahi, A., Aydin, S., Ince, B., Ince, O. (2016). Evaluation of microbial population and functional genes during the bioremediation of petroleum contaminated soil as an effective monitoring approach. *Ecotoxicology and Environmental Safety*, 125, 153-60.

Suja, F., Rahim, F., Taha, M.R., Hambali, N., Razali, M.R., Khalid, A., Hamzah, A. (2014). Effects of local microbial bioaugmentation and biostimulation on the bioremediation

of total petroleum hydrocarbons (TPH) in crude oil contaminated soil based on laboratory and field observations. *International Biodeterioration and Biodegradation*, 90, 115-22.

U.S Environmental Protection Agency (1989). *Protocols from short term toxicity screening of hazardous waste sites*, EPA 600/3-88/029, Environmental Research laboratory. Corvallis, OR.

Wu, M.L., Dick, W.A., Li, W., Wang, X.C., Yang, Q., Wang, T.T., Xu, L.M., Zhang, M.H., Chen, L.M. (2016). Bioaugmentation and biostimulation of hydrocarbon degradation and the microbial community in a petroleum contaminated soil. *International Biodeterioration and Biodegradation*, 107, 158-64.



Sowing Qualities of Seeds from Selected *Robinia pseudoacacia* L. Clones

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Abstract

Aim of this study is to analyse the sowing qualities from six selected *Robinia pseudoacacia* L. clones from the seed orchard on the territory of State Forest Enterprise Parvomay (Plovdiv district). Laboratory and soil germination, energy of germination and sowing norms were investigated. Results show difference in the investigated indices between the separate clones, which probably are genetically determined. Soil germination is with about 18% lower than the laboratory one. Clones suitable for production of black locust seedlings are Jazzkiseri, Appalachia and Pordim-4, whose genetic settings provide higher germination qualities of seeds compared to the rest of the clones.

Keywords: black locust, clone, half-sib progeny, germination

Introduction

Black locust (*Robinia pseudoacacia* L.), which is multipurpose tree species, is assessed lately in many countries worldwide as one of the perspective species for production of biomass and energy plantations grown at higher density and short rotation (Gyuleva et al., 2013; Gyuleva, 2014; Geyer, 2006; Rédei et al., 2010, 2011).

The first black locust seed orchards in Bulgaria have been established in the 1980s, which has put the black locust management on a scientific basis (Donchev, 1989). Along with the development and improvement of a technology for vegetative propagation of the species with root cuttings (Naydenov et al., 1989; Broshtilov et al., 1998), the clonal frame for this species was introduced. Tsanov et al. (1992) publish the first results from testing the vegetative progenies of 34 selected black locust clones from 6 populations in North Bulgaria.

From the established plantations and orchards, forest reproductive material is obtained today, from which seedlings with valuable qualities are produced for the needs of forestry.

According to data from the laboratory of the Forest Seed-control Station in Sofia, decreasing of the vitality of black locus seed lots, originating from various regions of Bulgaria, is observed in the last 10 years. The literature review made for this study shows that there are no particular investigations of the sowing qualities of *Robinia pseudoacacia* L. seeds for the mentioned period. Similar investigations during the period from the 1950s until today are mainly directed to the ways of pre-sowing preparation of black locust seeds (Stefanov, 1951; Velkov, 1968; Mirzaei et al., 2013; Basbag et al., 2010; Abdullah et al., 2019; Christin et al., 2019).

The aim of this study is to analyse the sowing qualities of *Robinia pseudoacacia* L. seeds from six selected clones from the seed orchard on the territory of State Forest Enterprise Parvomay (Plovdiv district), which have shown good results according to growing indices at testing of their vegetative progenies in previous investigations (Tsanov et al., 1992).

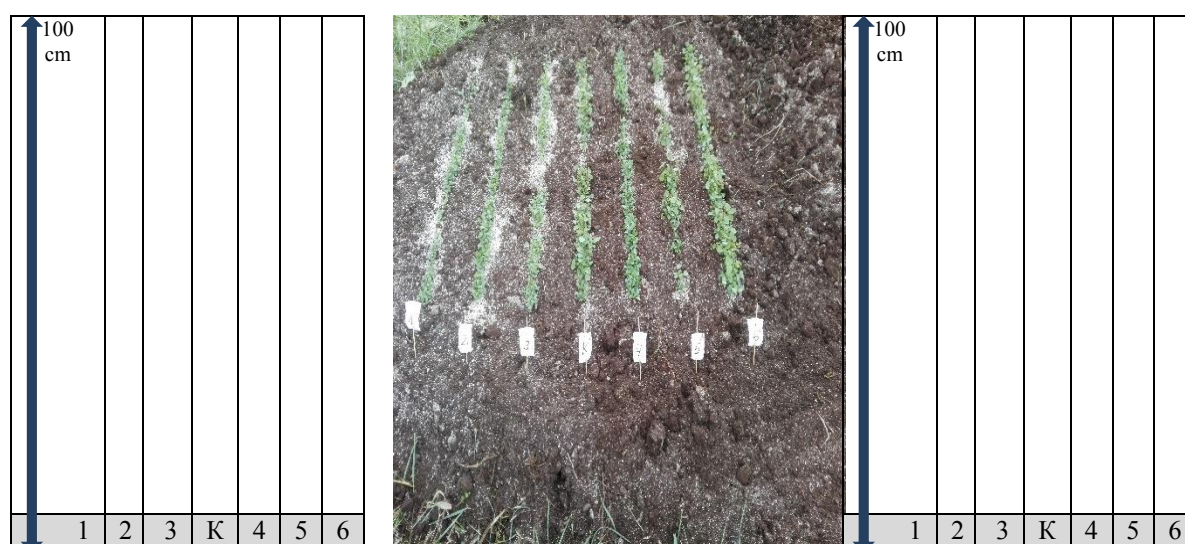
Materials and Methods

Objects of investigation are seeds from six selected *Robinia pseudoacacia* L. clones, collected from vegetative seed orchard of State Forest Enterprise Parvomay next to Mechka reka nursery. The orchard was established in 2004 at a scheme 8x8 m and includes 37 clones. For the control, a total collection of seeds is used with provenance from vegetative seed orchard located in the forest nursery Lukovit (State Forest Enterprise Lesidren).

Laboratory sowing qualities of the obtained seeds were tested in the Forest Seed-control Station – Sofia according to the ISTA method.

For determining of the soil germination of clones, an experiment in the forest nursery Lokorsko was carried out in seed rows– in 3 repetitions at a scheme shown on figure 1. The seed rows includes 7 rows with a length of 1 m and a distance of 10 cm between the rows in which seeds are sown according to the scheme of each clone. Sowing was made on 15 May according to the norms established by the Forest Seed-control Station – Sofia. Results were checked every 5th day, and the last one was on 5 June.

Pre-sowing preparation of the black locust seeds was made after the method of three times dipping in hot water followed by cooling. This method has been recommended as efficient and safe (Stefanov, 1951; Velkov, 1968; Mirzaei et al., 2013; Basbag et al., 2010; Abdullah et al., 2019; Christin et al., 2019). With the aim of better scarification, ice has been added to the cooling water.



Legend: 1 – clone Pordim 4; 2 – clone Jaszkeseri; 3 – clone Oryahovo 5; 4 – clone Appalachia;
5 – clone Pordim 1; 6 – clone Ryahovo 7; K – control

Fig. 1. Sowing scheme of black locust seeds in seed rows

Sowing was made in an universal substrate with the characteristics: medium fraction (0 - 40 mm), composition (in 250 l scale: 70 % bright peat 0 - 40 mm, 30 % black peat 0 - 40 mm, 1 kg NPK 14-16-18, 50 g trace elements and Tenzid – moisturising agent, pH 5,5 - 6,5).

The sowing rate is determined according to the formula from Annex №7 of the Ordinance №4 from 15.02.2012 on the terms and conditions for registration of forest nurseries, as well as for the production of seedlings in forest nurseries – state property.

$$D = 10 \cdot O \cdot M / C \cdot G_s \cdot K, \text{ where}$$

D – density of the sowing

O – optimal number of ponies per 1 m (number of annual seedlings according to Annex №7 of the Ordinance №4 + 20%reserve for waste)

G_s – germination of seeds from the batch

M – mass of 1000 seeds from the batch

C – purity of the seeds in %

K – correction factor for soil germination of seeds (<1, established experimentally)

Results and Discussion

The management of genetic resources of forest tree species and their efficient conservation depend on sowing qualities of seeds, which differ at various provenances of many species from family Fabaceae, including black locust (Rajora, Mosseler, 2001; Tozer, Ooi, 2014; Safdar et al., 2021; Andrea et al., 2022).

After carrying out of analyses of sowing qualities of clone lots and the control it was established that the average mass of 1000 seeds varies from 17.5 to 22.7g. The laboratory germination is with average value 31.9% and varies from 7% to 59%. With highest germination are seeds from clones Jazzkiseri and Appalachia, and the first one is with 12% more, and the second one – with 27% lower than the control (52%). The energy of germination on the seventh day (E_{к7}) varies from 6 to 54%, and its average value is 28.7% (table 1).

On the basis of physical characteristics and laboratory germination, sowing norms of the lots of different clones were determined; they are shown on table 1. The index values vary in wide range – from 0,96 to 8,25 g/m. The average value of the sowing norm is 2,7 g/m. Correlation between germination and seeds mass was not determined.

Obtained results show that with highest soil germination are clones Jazzkiseri and Appalachia, the first one being with 14% higher and the second one – with 31% lower than the control (45%). The average soil germination is 26,3%. Germination of seeds begins between the 5th and the 10th day from the start of sowing and ends up to the 20th day. Percent of the germinated seeds on the 20th day varies from 5 to 52%, and its average value is 26,3 % (table 2). The dynamics of seeds germination, however, is different for the various clones and this aspect should be taken into account at the providing of reproductive material in connection with the final aim (Giuliani et al., 2019).

Table 1. *Qualities of sowing materials according to clones and control in laboratory conditions*

Clone from <i>Robinia pseudoacacia</i> L.	Location (forest enterprise)	Kind of source	Kind of seed analysis	Index				
				Purity	Abs. mass	Laboratory germination	Ек7	Sowing norm
				%	G	%	%	g/m
<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>
Pordim – 4	Plovdiv/ Parvomay	Vegetative seed orchard	Germination after scarification	99	19,9	31	24	1,63
Jazzkiseri	Plovdiv/ Parvomay	Vegetative seed orchard	Germination after scarification	99	19,8	59	54	0,85
Oryahovo – 5	Plovdiv/ Parvomay	Vegetative seed orchard	Germination after scarification	99	17,5	21	20	2,12
Pordim – 1	Plovdiv/ Parvomay	Vegetative seed orchard	Germination after scarification	99	22,7	7	6	8,25
Ryahovo – 7	Plovdiv/ Parvomay	Vegetative seed orchard	Germination after scarification	99	20,7	15	13	3,51
Appalachia	Plovdiv/ Parvomay	Vegetative seed orchard	Germination after scarification	99	20,7	38	35	1,39
Control	Lukovit	Vegetative seed orchard	Germination after scarification	99	19,6	52	49	0,96
Average values:				99	20,1	32	28,7	2,7

It is seen from the analysis that the laboratory and soil germination of seeds is highest for the clones Jazzkiseri, Appalachia, Pordim-4 and the control. The applied multi-rank Duncan criterion identifies well-expressed and statistically significant differences in the average values of the laboratory germination of seeds in various clones ($F=855.400$, $df=6$, $Sign. = 0.001$), and the same one is observed in the soil germination, as well ($F=890.714$, $df=6$, $Sign.= 0.001$).

Table 2. Qualities of sowing materials according to clones and control in seed rows

Clone from <i>Robinia pseudoacacia</i> L.	Location (forest enterprise)	Kind of source	Kind of pre- sowing preparation	Index						
				Purity	Abs. mass	Soil germination	Date of report			
							15 May	20 May	25 May	31 May
							Percent of germination according to days; date of establishment 15 May			
				%	G	%	E5 %	E10 %	E15 %	E20 %
<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>10</i>	<i>11</i>
Pordim – 4	Plovdiv/ Parvomay	Vegetative seed orchard	scarification	99	19,9	24	0	19	21	24
Jazkiseri	Plovdiv/ Parvomay	Vegetative seed orchard	scarification	99	19,8	52	8	38	47	52
Oryahovo – 5	Plovdiv/ Parvomay	Vegetative seed orchard	scarification	99	17,5	16	0	9	14	16
Pordim – 1	Plovdiv/ Parvomay	Vegetative seed orchard	scarification	99	22,7	5	0	3	5	5
Ryahovo – 7	Plovdiv/ Parvomay	Vegetative seed orchard	scarification	99	20,7	11	0	9	11	11
Appalachia	Plovdiv/ Parvomay	Vegetative seed orchard	scarification	99	20,7	31	3	18	29	31
Control	Lesidren/ Lukovit	Vegetative seed orchard	scarification	99	19,6	45	6	36	43	45
Average:				99,0	20,1	26,3	5.7	18.9	24.3	26.3

This presumes the existence of a correlation between the seeds provenance for both types of germination, which probably are genetically determined.

In case that these clones are used for seedling production, of an interest would be also the testing of qualities of their half-sibs progenies with a view to obtain qualitative sowing material.

Conclusion

The analyses of sowing qualities of seeds from selected *Robinia pseudoacacia* L. clones in the present study showed that there is a correlation between the seeds provenance and their laboratory and soil germination.

Soil germination is about 18% lower than laboratory germination, which shows that the applied pre-sowing preparation and the selected substrate for sowing are the right ones and have provided optimal conditions for seeds development.

Clones Jazskiseri, Appalachia and Pordim-4 are suitable for the production of black locust seedlings, whose genetic endowments provide higher germination qualities compared to the rest of the clones. *Robinia pseudoacacia* L. is propagated both by seed and vegetatively. The methods of vegetative propagation may to be applied to these clones. Depending of the purpose for which the plantations are created, seed production of seedlings is much easier and cheaper method.

References

- Abdullah, K. H., Ahmed, G. B., Selah-Alden, M. T., Hassan, H. N., Mahmood, M. J., Hammed, N. A., Amin, S. M. (2019). Overcomming Seed Dormancy of *Robinia pseudoacacia* L. and *Ceratonia siliqua* L. Species Using Different Pretreatments in Malta Forest Nursery – Duhok. Journal of Duhok University, 21 (1), 1-7. (in Turkish)
- Andrea M. R., Truta, A. M., Viman, O., Morar, Irina M., Velibor, L., Spalevic, C. D. , Sestras, R. E., Holonec, L., Sestras, A. F. (2022). Seed Germination and Seedling Growth of *Robinia pseudoacacia* L. Depending on the Origin of Different Geographic Provenances. Diversity, 14, 34. Published: 6 January 2022, 15p.
- Basbag M., Aydin A., Ayzit, D. (2010). The Effect of Different Temperatures and Durations on the Dormancy Breaking of Black Locust (*Robinia pseudoacacia* L.) and Honey Locust (*Gleditsia triacanthos* L.) Seeds. Not Sci Biol 2 (4), 125-128.
- Broshtilov, K., Kalmukov K., Tsanov Ts., Y. Naydenov. (1998). Vegetative propagation of Black locust (*Robinia pseudoacacia* L.). – In: International Plant Propagators Society. IPPS in Bulgaria – Third Scientific Conference Propagation of Ornamental Plants, Forest University, October 3-5, Sofia, 167-173. (in Bulgarian)
- Christin, C., Lehmann, J., Landgraf, D., Pretzsch, H. (2019). *Robinia pseudoacacia* L. in Short Rotation Coppice: Seed and Stump Shoot Reproduction as well as UAS-based Spreading Analysis. Forests 2019, 10, 235-258; doi:10.3390/f10030235
- Donchev, Zh. (1989). Technology for establishment of intensive black locust plantations. Report on a project on contract with the Committee of Forests. (in Bulgarian, unpublished)
- Geyer, W. A. (2006). Biomass production in the Central Great Plains USA under various coppice regimes. – Biomass and Bioenergy, 30, 778-783.
- Giuliani, C., Lazzaro, L., Calamassi, R., Fico, G., Foggi, B., Lippi, M.M. (2019). Induced water stress affects seed germination response and root anatomy in *Robinia pseudoacacia* (Fabaceae). Trees, 33, 1627–1638.
- Gyuleva, V., Stankova, T., Popov, E. (2013). Establishment of plantations of fast-growing tree species in Bulgaria with a short rotation for energetic purposes. – Science&Technologies, 3 (6), 96-100. (in Bulgarian)

Gyuleva, V. (2014). Selection and testing of fast-growing tree species for accelerated production of wood raw material – preliminary results from sample plots in Zlatna Panega. – In: Proceedings of scientific publications of the Forest Research Institute, 145th anniversary of the Bulgarian Academy of Sciences, S., 239-245. (in Bulgarian)

Mirzaei, M., Moghadam A.R. L., Ardebili Z. O. (2013). The induction of seed germination using sulfuric acid, gibberellic acid and hot water in *Robinia pseudoacacia* L. International Research Journal of Applied and Basic Sciences, Vol. 4(1), 96-98. ISSN 2251-838X

Naydenov, Y., Tsanov, Ts., Broshtilov, K., Kalmukov, K. (1989). Vegetative production of black locust seedlings. – Lesovadstvo, 2, 3-4. (in Bulgarian)

Ordinance №4, Annex №7 from 15.02.2012 on the terms and conditions for registration of forest nurseries, as well as for the production of seedlings in forest nurseries – state property. Ministry of Agriculture and Food.

Rajora, O.P.; Mosseler, A. (2001). Challenges and opportunities for conservation of forest genetic resources. Euphytica, 118, 197–212.

Rédei, K., Viperdi, I., Tome, M., Soares, P. (2010). Black Locust (*Robinia pseudoacacia* L.) Short-Rotation Crops in Hungary: A Review. – Silva Lusitana, 18 (2), 217-223.

Rédei, K., Csiha, I., Keseru, Zs. (2011). Black locust (*Robinia pseudoacacia* L.) Short-Rotation Crops under Marginal Site Conditions. – Acta Silvatica and Lignaria Hungarica, 7, 125-132.

Safdar, M.E., Wang, X., Abbas, M., Ozaslan, C., Asif, M., Adnan, M., Zuan, A.T.K. Wang, W., Gasparovic, K., Nasif, O. et al. (2021). The impact of aqueous and N-hexane extracts of three Fabaceae species on seed germination and seedling growth of some broadleaved weed species. PLoS ONE, 16, e0258920.

Stefanov, B. (1951). Hard seeds of leguminous plants. Proceedings of the Biological Institute, vol. II, 3-43. (in Bulgarian)

Tozer, M.G.; Ooi, M. (2014). Humidity-regulated dormancy onset in the Fabaceae: A conceptual model and its ecological implications for the Australian wattle *Acacia saligna*. Ann. Bot., 114, 579–590.

Tsanov, Ts., Naydenov, Y., Kalmukov, K., Broshtilov, K. (1992). First results from testing of some black locust clones. – Nauka za gorata (Forest Science), 4, 24-30. (in Bulgarian)

Velkov, D. (1968). Influence of high temperatures on the water regime and viability of black locust (*Robinia pseudoacacia* L.) seeds. In Proceedings of the International Symposium on Seed Physiology of Woody Plants at Kórnik, Panstwowe, Wydawnictwo Naukowe, Warszawa-Poznań, Poland, 3–8 September 1968; pp. 111–119. (in Russian)



112 Years Since the Foundation of Soil Science and 110 Years Since the Foundation of the Soil Institute in Bulgaria



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Abstract

Historical soil science is called to analyze and evaluate realistically and critically the role of important dates and discoveries that determine the further development of soil science. Of particular importance for soil science is the first scientific and fundamental work of N. Pushkarov "Formation of the soil", published 112 years ago.

With the present work an analysis of the natural and philosophical-dialectical interpretations of his work related to the genesis of the soil is made. Pushkarov applies the genetic approach to the study of soils and refutes the so-called. agro-geological (geological) approach, which dominated at that time in world soil science. He makes an accurate and objective general assessment of the factors and conditions of soil formation and proves new knowledge of methodical and fundamental nature, which is applied in further research in the country. At the same time, facts are presented about the soil science or agro-geological section established by him in 1911, which performs the tasks for soil-cartographic research formulated by him. All this gives grounds to conclude that in 1909 N. Pushkarov laid the foundations of soil science in Bulgaria, and in 1911 he established a scientific-administrative unit (scientific organization at the section level) and laid the foundations of the Institute of Soil Science. .

Keywords: Nikola Pushkarov, soil science, soil science section, genetic approach, genesis, agro-geological bias, analysis and evaluation

Introduction

Two important scientific events in Bulgarian soil science, related to the name of the great Bulgarian natural scientist, soil scientist, public figure, patriot and revolutionary Nikola Pushkarov deserve to be objectively analyzed and evaluated due to the fact that they are extremely important for the development of soil science we have. There are scientific and literary sources and facts about both events, which are irrefutable proof that one event has a purely scientific and fundamental character, and the other - scientific and administrative. It is difficult to say which of them is more important, as both have their place in the development of Bulgarian soil science. In the order of the search for historical truth and the requirements of science, it is right to give priority to the first scientific event, which aims to prove the genetic nature of the origin of the soil. In fact, this is the first scientific work of N. Pushkarov,

published in the journal "Natural Science", book 8, pp. 481-489, 1909-1910, which applies Dokuchaev's approach and principles for scientific consideration of soil and soil formation. It is an indisputable fact that with this work the science of soils in our country was born and founded. No less important is the second event, which with the establishment at the suggestion of Pushkarov of a scientific-administrative organization in 1911 (soil or agrogeological section) at the State Agricultural Experimental Station in Sofia, laid the foundations of the Soil Institute in Bulgaria. With the comprehensively developed research program, he began to conduct the first soil surveys throughout the country. The distinction between these two events in role and significance is obligatory in the name of historical truth.

What are the goals and objectives of this study?

In connection with the above, the present study has the task to ask two important questions: First: to clarify the beginning of the founding of soil science in Bulgaria by studying the pedogenesis of Pushkarov and second: to distinguish this beginning from the time of the first scientific administrative unit. soil-geographical, soil-cartographic and soil-agrochemical studies in the country in 1911, which is incorrectly considered to be the birthplace of Bulgarian soil science. For this purpose, a thorough analysis and evaluation of the natural-scientific and philosophical-dialectical interpretations of his work, related to important for soil science, unexplained issues, namely: definition of soil, establishing its genesis, factors and conditions of soil formation, of the main and most general circular processes that take place in it and last but not least - upholding the genetic approach to the study and formation of soil.

Historical period of writing the scientific work by Pushkarov

Pushkarov's scientific article is still relevant today and is of lasting importance for both Bulgarian and world soil science. It was written when world soil science sets and determines the approaches, methods and directions of development of soil science. It is dominated by the influence of agro-cultural chemists and agro-geologists, who develop the agro-cultural and agro-geological bias in soil science. As a geologist-naturalist, Pushkarov began his first research as such and contributed to the petrography of the high Balkans between the peaks of Yildiz Tabia and Vezhen in 1902. As a soil scientist, however, he later became a successor to the soil genetic approach then unknown in us (until 1902) and founded in 1883 in Russia (Dokuchaev, 1883; Pushkarov, 1909). This is clearly evident in his first scientific work in the field of soil science and soil geological essays, which he later developed.

Scientific analysis and evaluation of scientific labor

The article, which is of fundamental importance for our science, begins with his famous thought "The ray gave life, and the earth - the material basis of this life." On this basis, he reveals some natural-genetic and his philosophical (dialectical) judgments about the identical nature of matter and motion, the vital motion of solar energy and earthly parts and the transformation of inanimate matter into living and vice versa. Describes the material (chemical) elements and compounds of living and non-living bodies - O, H, C, N, Fe, S, Ca, Mg, gases, oxides, acids and others that are the basis of soil formation of the earth's crust, respectively. soil and constantly enter into "new relationships" and "new groups".

What is Pushkarov's definition of soil? In metaphorical language, he gives a very interesting definition of the soil, namely, "The soil is the vast laboratory where the preparation

of dead matter takes place in order to enter the cycle of life. Soil is a living layer of the globe. Like a thin, delicate diaper, it covers the vast body of the earth and gradually spiritualizes that body. With this definition, Pushkarov approached the doctrine of the noosphere before Vernadsky (2009) created it. All these interpretations so far show that he considers the soil as a living biological system, as part of the biosphere, which is essentially a planetary phenomenon of a cosmic nature. Pushkarov gives a spiritual essence to the soil. Man, as part of the biosphere, is the one through whom every natural body on Earth can be spiritualized. Man is the thinking layer of the planet Earth and his role is to cultivate or destroy soils (Teoharov, 2017). It is noteworthy that Pushkarov emphasizes the role of chemistry and its thousands of evidences for studying the cycle of elements and substances and the eternal transition of living to inanimate matter and vice versa.

The role of conditions and factors in soil formation

When describing the factors and conditions of soil formation, of course, as a geologist, he points out in the first place the importance of rocks in the course of soil formation processes, without defining them as a primary factor. For him, all factors and conditions are equally important in soil formation. Pushkarov believes that there is a constant exchange between the soil and the rock (hard crust) and the latter is the primary source of mineral composition and movement. He points out that the oxidation of minerals in nature is a process that takes place every minute. The result of this process are many metamorphic rocks and minerals. Therefore, the rocks form new rocks, and hence new modern soils. It takes into account the local nature of the rocks, which is still used as a diagnostic indicator at the generic taxonomic level in the classification of soils in almost all schools. According to Pushkarov, their local features may change under the influence of applied soils outside the location. As a representative example he gives the Cretaceous limestones covered with loess cover in the Danube plain. He considers the thick layers of rocks in the plain as former soil, which was carried away and deposited in the water basins gradually during the geological epochs. Later, our scientists confirmed the spread under the loess of the so-called. buried soils (Minkov, 1968). Considering the question in this way, it can be concluded that much earlier than other scientists, in practice, he indirectly came to the theory of large and small geological (biological) cycle of elements and substances. In his further work in soil-cartographic research, Pushkarov described in detail the influence of rocks on soil formation and linked geological processes with soil-forming. This is proof of the extensive training he achieved in the early years, thanks to the fact that he had the opportunity to be guided, scientifically and critically evaluated by his professor, Academician Georgi Bonchev - the first Bulgarian petrographer and mineralogist. Along with him and other geologists, he was one of the founders of the Bulgarian Geological Society (Kolarova, 1959). Even today, soil science cannot develop without the knowledge of petrography, mineralogy and geochemistry, and Pushkarov applied these sciences in soil science with great competence. He considers the flora and fauna as important sources and factors for the formation of the soil (after the rocks). He called animals in the soil "organized inhabitants", noting some living organisms that are an integral part of it, without which it loses much of its basic character - to serve as a link between dead and living matter. It also emphasizes the biochemical, physical and physico-chemical factors of soil and nature. Pushkarov connects organisms (lower, higher), the root system of plants, organic residues, water and temperature with weathering (rock breaking)

and soil formation processes. He points out the role of water (atmospheric, rain, flowing, local, erosional) on weathering and soil formation, its composition and movement, mechanical and physical impact on minerals, rocks and organic matter. Some of his thoughts on its significance for the pedosphere, flora and fauna deserve attention. "The soil is the upper layer of the earth's crust, where the roots of plants are located and where animals find shelter and food. Soil that does not contain water is dead soil. It is the only solvent from which plants can draw mineral salts for their growth. Pushkarov describes its role in the formation of various geomorphological forms, and thus changes in the earth's surface, in general relief and topography. His example from the Balkans is remarkable, where he points out that "with its centuries-old work the water has cut the Balkan Mountains". He pays special attention to the movement of winds, emphasizing that it is the strong winds that polish and give different shapes to the rocks. As typical examples he points out the Belogradchik rocks, those along the Iskar gorge, the Stone forest near Gebedje and others. In this way he indirectly defends the "Aeolian hypothesis" for the formation of the most fertile fields in Europe - the Danube, Rhine, Yellow River and others. Pushkarov, albeit briefly, addresses the issue of anthropogenic activity and changes in its soil. Using folk memory, he gives a concrete example of the degradation of soil by man. He writes: "Old people claim that the Slivnitsa and Dragoman heights were covered with forests and after the destruction of the latter nothing can grow on the bare rock." Later, Acad. Ivan Stranski confirmed the same processes of deforestation and anthropogenic transformation of soils that took place after the felling of oak forests in the Sofia field.

The analysis of the scientific work shows that Pushkarov strictly methodically and consistently applies the genetic approach in the study of genesis (soil origin). Almost all of his views are further embedded as an alphabetical truth in a number of works, textbooks and manuals.

How does the agrogeological field of soil science study the genesis of soils at the same time?

This work appears to be fundamental in the science of soils in Bulgaria. We will take advantage of additional facts proving its scientific and fundamental importance. To this end, we will make a brief comparative analysis of the approaches applied at the same time by some other soil schools. We will not dwell on the Dokuchaev doctrine, which, as we know, applies the genetic approach to the study of soils and its influence, albeit at a later stage, on world soil science. When Pushkarov published his work, the agro-cultural and agro-geological direction of studying the genesis of soils developed in Germany, which spread to a number of countries in Europe and America (Gerasimov, 1985). At the beginning of the twentieth century, some scientists in our country adhered to these approaches, without having in-depth developments (P. Berov - agronomist and G. Bonchev - geologist). It is important to know that agrogeology considers the soil as a geological formation, inert body, weathering material, which contains nutrients obtained from weathering of rocks. According to agrogeologists, the soil is considered as a weathering crust, and the process of soil formation - as a process of weathering (Gyurov, Kolcheva, 1969). In 1922, the Third International Conference on Pedology was held in Prague, attended by 14 countries, incl. and USA. It decided to detach soil science from the agrogeological slope and adopted the Dokuchaev approach to the study of soils (Stranski, 1946; Teoharov, 2016). Thus, the genetic approach to the study of

pedogenesis began to dominate in world soil science and factor-process, profile-evolutionary, horizon-profile, profile-specific (process) and evolutionary diagnostics of soils gradually became established; Clayden B. and JMHollis, 1984; Aubert G., 1988; Shishov et al., 2004; FAO, 2014). All this is proof of the relevance of Pushkarov's scientific work and its enduring significance. Through it he proves new knowledge of a fundamental nature, making an objective assessment of the main factors and conditions of soil formation that determine the genesis of soils and thus refutes in theory and practice the agrogeological approach in soil science. Thus Pushkarov, through this work, appeared as the founder of soil science in Bulgaria in 1909. Without making a detailed analysis, a similar opinion was expressed by Prof. E. Kolarova (1959). She writes: "In our opinion, this is the first article that scientifically examines the issues of soil and soil formation in our special literature. Moreover, this scientific article was written at the level of science not only at that time, but also of modern science - soil science. It is inexplicable why no one pays attention to this scientific assessment of Pushkarov's work, and all soil scientists point to 1911 as the "birth" of Bulgarian soil science. Another cardinal question arises from the exposition made - What was then the year of birth of Bulgarian soil science - 1909 or 1911? The annual report for 1910-1911 of the State Agricultural Experimental Station - Sofia reads as follows: "Ministry of Trade and Agriculture, aware of the great need for comprehensive study of soils in the country opened a new section at the station, very important for our agriculture agrogeological, appointing on 17.09. the same year and a person with the appropriate preparation for its filing "(Naidenov, 1913). This person is Nikola Pushkarov, who makes a proposal to the Minister to open a section on soil science. In practice, the section headed by Pushkarov is a scientific-administrative unit with an independent plan and tasks. In the reports on its activity he develops and sets for implementation the following program tasks: 1. Systematic study of soils by regions, for which purpose geological, biological and climatic data are collected and the collected samples are analyzed chemically and physically. 2. Finding out the reasons for the change of the properties of the soils in a given place and indicating as much as possible the means for elimination of the adverse phenomena. 3. Making maps for the studied areas. With their general formulation, these program tasks are still relevant today. These tasks give us reason to believe that they are strictly fundamental and applied. These are well-formulated tasks with a visible perspective for obtaining new knowledge and solutions for practice. They were adopted by the Ministry of Trade and Agriculture and their implementation began immediately. In 1913 the first soil-geological sketch with agrogeological map in M 1: 26000 for the Sofia field was printed, developed independently by Pushkarov. According to Acad. Gerasimov (1985), the essay "is a valuable scientific monograph". In this work the opinion about the soil as a product of the combined influence of a number of natural factors is developed, which he clarifies in his work "Soil formation". Acad. Gerasimov also notes that this opinion is much broader and correct than previous agrogeological ideas in soil science.

Conclusion

"Soil formation" is the first scientific work in Bulgaria, in which Pushkarov clarifies the genesis and nature of soils, sets the principles of the genetic approach to their study and refutes the agrogeological (geological) direction in soil science. He makes an accurate and objective assessment of the conditions and factors of soil formation and proves new

knowledge of a methodical and fundamental nature, which still has its current relevance. With the developed program tasks and the soil science section created on his proposal, he applies this approach and the new knowledge in science and practice. All this is proof that Pushkarov founded soil science in 1909, and through the scientific and administrative organization he created at the section level in 1911, he laid the foundations of the Institute of Soil Science.

References

- Vernadsky V.I. (2009). *Scientific thought as a planetary phenomenon*. Ed. Acad. S. Ganovski, S., 246 p.
- Gerasimov, I. (1985). *Fundamental scientific problems of modern Dokuchaev soil science*. Zemizdat, S., 92 p. (in Bulgarian)
- Gurov G., Kolcheva, B. (1969). *Soil science*. Ed. Hr. G. Danov, Plovdiv, 368 p. (in Bulgarian)
- Dokuchaev, V.V. (2008). *Russian chernozem*. Ed. Russian Collection, St. Petersburg, 473 p. (in Russian)
- Kolarova, E. (1959). Essay on the life and scientific activity of NP Pushkarov. In: *Nikola Petkov Pushkarov*, Izd.BAN, S., 11-26. (in Bulgarian)
- Minkov, M. (1968). The fate of Northern Bulgaria. Ed. BAS, 2020 p. (in Bulgarian)
- Naidenov, V. (1913). Annual report of the station for 1910 and 1911. G. Gavazov Printing House, Sofia, 57 p. (in Bulgarian)
- Pushkarov, N. (1909-1910). Soil formation. *Mr. Natural Science*, Book 8, 481-489 (in Bulgarian)
- Stranski, Iv. (1946). *Soil Science*. University Printing House, Sofia, 585 p. (in Bulgarian)
- Stranski, Iv. (1974). The Black Soils of Sofia. In: Ivan Stranski - *Selected works*, ed. BAS, S., 11-59. (in Bulgarian)
- Teoharov, M. (2017). Soil science - the science of the past, present and future. In: *World Soil Day, December 5, 2016*. Ed. BPD, S., 18-34 (in Bulgarian)
- Shishov, L.L., Tonkonogov V.D., Lebedeva I.I., Gerasimova, M.I. (2004). *Classification of soils in Russia*. Smolensk, Oikumena, 343 p. (in Russian)
- Aubert G. (1988). *Referentiel Pedologique Francais*. Orleans, 2nd Proposition, INRA, 251p.
- Clayden, B. and Hollis, J.M. (1984). *Criteria for differentiating soil series*. Technical monograph, N 17, Harpenden, 159 p.
- FAO, (2014). *World reference base for soil resources*. By: IUSS-ISRIC-FAO, World soil resources reports, N 103, Rome, 203 p.

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Citation and References

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Journal articles

- Atanassova, I., Doerr S. (2010). Organic compounds of different extractability in total solvent extracts from soils of contrasting water repellency. *European Journal of Soil Science*, 61(1), 298-313.
- Calderón, H. W. (1982). The content and composition of humus in arid alluvial soil of Peru. *Soil Science, Academy of Sciences of USSR*, Moscow, 8(1), 53-59. (in Russian).

Books

- Sparks, D. L. (2002). *Environmental Soil Chemistry*, 2nd Edition, Academic Press, San Diego, CA.
- Lidanski, T. (1998). *Statistical methods in biology and agriculture*. Zemizdat, Sofia (in Bulgarian).

Book chapters or conference proceedings

- Maison, S. P. (1993). Advanced soil remediation. In: *Plants that accumulate heavy metals* (P. D. Tox, ed.). CAB Int., Wallingwood, USA, 291-307.
- Kostov, D., Radev, H. Peeva, M. (2008). Study of newly introduced cultivars of green and red apples. In: *Sustainable Fruit Growing: From Plant to Product, Proceedings of International Scientific Conference, Bulgaria*, 46-53.
- Petrova, R. (1989). Loss of Humus Soil in the Process of Reclamation of Damaged Terrains. In: *Fourth National Conference on Soil Science 'Problems of Soil Science in Intensive Agriculture'* (N. Sherbanova, R. Nacheva, Eds.). BSSS, N. Poushkarov Soil Science and Yield Programming Institute, Sofia, 203-206, (In Bulgarian).

Online publications

Lecoq, H. & Desbiez, C. (2012). Viruses of cucurbit crops in the Mediterranean region: an ever-changing picture. *Adv. Virus Res.*, 84, 67-126. <http://doi.org/10.1016/B978-0-12-394314-9.00003-8>.

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